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AUTOMATIC PROCESS MONITORING

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AUTOMATIC PROCESS MONITORING*

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FOREWORD

Andres Ferrari
Technicon Instrument Corporation, Chauncey, N.Y.

In recent years the great advances in instrumentation and our increasing industrial requirements have brought to the fore the necessity of monitoring many of our industrial processes. For this reason it was felt that a monograph dealing with the subject of automation in process monitoring was mandatory.

Sidney Siggia, who is well known for his many articles on analytical problems, was asked to organize the conference on which this publication is based. Through his tireless efforts this monograph has been made possible. The contributors he chose and the topics they explore are of great interest and significance in this field.

INTRODUCTION

Sidney Siggia
Olin Mathieson Chemical Corporation, New Haven, Conn.

In the operation of a chemical process it is essential to maintain proper analytical control to make certain that all phases of the process are proceeding as they should. Thus in most chemical operations the starting materials are monitored for the content of the desired component, since the final yield of product will be based on this value. Also monitored are the various possible contaminants in the starting material that can be deleterious to either the chemical process or the final product. Some such contaminants could be catalyst poisons; reaction inhibitors or accelerators; materials that contribute to hazardous conditions (explosives, pyrophoric materials, or toxic substances); materials that give an undesirable odor, color, or particle size to the final product; and materials that affect the yield ratio of product to by-products.

In addition to the starting materials, the materials at each stage of the process are monitored to make sure that that stage is going as it should and, finally, the end product is monitored to insure its meeting the necessary quality specifications.

Until fairly recently, the control of a process was carried out almost exclusively by manually sampling the plant stream and taking the sample to a control laboratory where an analysis was run by a chemist or operator using chemical or instrumental methods. The advantages of continuous, on-stream analysis over the older techniques are quite obvious.

Time. By the older approach, the sample must be taken from the stream and transported to the analytical location. There is a possible waiting period at the laboratory until an analyst is available to make the necessary measurements, and the methods of measurement usually involve a not insignificant length of time. During the time lapse between sampling and final measurement the process is continuing. If the process is not proceeding as it should, this will not be known until the analysis is finally obtained. By this time, a large amount of off-grade material can be produced or conditions undesirable in other ways may be allowed to exist for too long a time.

The continuous, on-stream analysis usually takes place in a few minutes and is often instantaneous, depending on the particular property being measured. When this method is used, there is relatively little time required for an analysis, and undesirable conditions are detected and corrected much sooner.

Ease of automation. The instrumental approaches used for continuous, on-stream analysis generally operate on the basis of a variation in signal that is detected on a dial or on a recorder. This same variation in signal can be used to actuate valves, compressors, pumps, and heaters to regulate the conditions necessary for correct operation of the process. In addition, these signals can actuate alarms or even shut down a process when hazardous conditions exist.

Handling of materials. It is often difficult to remove for transport a sample from a process stream or kettle. For example, an accurate sampling of a gas stream is difficult to obtain, and this operation can be entrusted only to responsible workers. More difficult to handle than gases are materials that are liquids in the process stream but gases at room conditions. Care must be taken in these cases to sample the liquid and not allow it to vaporize or fractionation of the sample will take place. Special containers have to be constructed to hold such materials and yet permit their transfer to analytical equipment. In addition, this type of material is usually kept cold to keep it in liquid form, and condensation takes place on all the equipment used for sampling. This can often introduce water into the sample during handling. In addition to the difficulty of sampling, the characteristics of the material also render it difficult to handle during analysis.

Some materials cannot be exposed to oxygen or sunlight because an alteration of the sample composition can be brought about by these agents. Other materials are processed at high temperature and solidify on sampling. This solidification in the sample container generally produces a fractional crystallization with the material near the walls being more pure than the material in the center. Such a sample has to be remelted before measured quantities are taken for analysis in the control laboratory.

Some materials are very toxic, corrosive, or otherwise dangerous to handle. Sampling procedures from a process stream in these cases have to be rigidly prescribed and carried out to avoid injury to personnel.

The on-stream analysis, however, requires no transfer of materials out of the processing equipment, and this eliminates such difficulties as those described before.

Minimizing error. The older control approach relies heavily on personnel. Sampling, measuring, taking readings, and calculation are done largely by laboratory workers. This type of operation is always subject to some human error, which is unavoidable and difficult to detect. A man may obtain a questionable analysis on a plant sample and may attain the correct answer on a known standard, yet this does not mean that the results on the plant sample are correct. With the type of approaches used for on-stream analysis there is little or no manipulation necessary. In general if the instrument reads correctly for the standard, then it is giving correct results on the plant stream. Periodic checks of on-stream analyzers are generally easily carried out by introducing a sample of known composition into the instrument.

Cost of operation. Continuous, on-stream analysis at first usually seems more expensive than the more classic control methods. This is due to the usual high initial costs of the instruments, installation, and modifications necessary to get the instrument to do the necessary job. Once the system is set up, however, operational expenses are generally lower for the on-stream approach since the number of operating personnel required to insure adequate plant control is lower than that required by the classic approach. Personnel, of course, is one of the largest items contributing to operating expenses. Another factor that has to be included in costs is that the continuous, on-stream approach yields more efficient analysis. The advantages gained as indicated above reflect savings in the over-all running of a chemical process.

The above paragraphs indicate the advantages of the type of analysis under discussion. It must be stated, however, that it is not possible to instrument all process streams because of certain chemical or physical conditions that are peculiar to the particular stream. In these cases we still have to rely on a control laboratory. As new instruments are devised, the range of application of continuous, on-stream analysis will continue to broaden. This does not mean the extinction of the process-control chemist but merely means a shift in emphasis from one set of tools to another and from one method of operation to another. The analyst is still very much in the picture in the on-stream approach since the analytical jobs have to be evaluated; the instruments have to be selected for the respective jobs; the instruments have to be set up to yield the desired data in the necessary ranges and with the necessary precision and accuracy; the day-to-day data has to be evaluated and interpreted in terms of the process under observation; and the quality of the analytical data turned out by the devices has to be insured by proper standardization at the necessary intervals.

Part I.

CONSIDERATIONS IN ESTABLISHING AND MAINTAINING AUTOMATIC ANALYSIS OF PROCESS SYSTEMS

T. L. Clift
Standard Oil Company of Ohio, Toledo, Ohio

Today, everywhere you go, process-and-control people are thinking, talking, and using continuous process stream analysis. This activity is making the continuous analyzer an increasingly important tool among the many tools available for control systems work. As with any other tool, we must give careful attention to why, when, where, and how continuous process stream analyzers are used. We must also keep our analyzers in good working order with a service factor as close to 100 per cent as possible. Let us review the considerations and techniques we use to get the best results in establishing and maintaining this important and relatively new tool.

Evaluation of Equipment

We do not install this type of equipment in our plants until it has been given a release from our evaluation program.

This program consists of installing the equipment, as it becomes available, in a portable trailer. The trailer is moved from plant to plant, and the equipment is placed in operation on a piece of process equipment calculated to have the most benefit. The trailer is manned with competent personnel having a good background in the chemistry involved, process operation, and instrument design.

The plant where this trailer is going to be set up has to be first approved by the plant manager. When this approval is given, the trailer personnel have certain authority, within limits, to change the operation of a piece of process equipment to prove the analyzer under test. As this test continues more and more is learned about the analyzer's accuracy, reliability, and problems.

During this period the trailer personnel work closely with the analyzer manufacturer and mutually try to solve all the problems that arise. As the progress continues to a point where the trailer personnel feel that this analyzer can become an instrument for plant use, we start sending our analyzer personnel from various refineries to start a training program on this particular analyzer. Since refinery personnel are going to be responsible for keeping the analyzer in continuous operation after it is placed in the plant, their arrival gives the plant personnel an early start in learning the equipment.

In this stage the plant personnel are able to see the final test and calibration of the analyzer and how it is coordinated with plant-control laboratory results. This particular area can be quite confusing if there is not good understanding and cooperation on the part of both the analyzer and laboratory personnel.

After final calibration and after the analyzer has proven its reliability, accuracy, and reproducibility, it is released as a reliable piece of equipment for plant use.

Application and Justification

It now becomes the responsibility of the operating department, process engineering department, and control systems department to survey all possible applications for the analyzer that has just been released and to find the best application with potentially the greatest calculated payout.

In our original justification, we keep in mind that a rejustification will take place approximately six months after the equipment has been in continuous operation. We have found that, if the right application has been selected, the equipment usually pays for itself in three to six months.

In rejustification, we have found that we were very conservative in our original justification. For the equipment to do what we cited above, the following points must be considered: (1) education of all personnel concerned; (2) selection of the right application; (3) selection of good workable equipment; (4) correct engineering and installation of the equipment and of all auxiliaries; (5) achievement and maintenance of correct calibration; (6) ascertainment that the cost of routine and preventive maintenance is part of the justification; (7) availability of adequate and properly trained manpower; and (8) assurance that operating personnel will accept and use the analyzer results.

Education

We start with trying to acquaint members of the top management with this equipment and explain to them why they should spend capital dollars for it. This sum is considerably more than they have been accustomed to spend in order to get information about their operating units. However, when we explain to them the possible return on the dollars spent and when management gets the feedback on the results, the next application is not so hard to sell. In fact, management soon becomes the driving force to get more and more of this equipment into use.

Naturally the more of this equipment that is installed the harder it becomes to find applications with the fantastic payouts experienced in the original installation.

The introduction of the analyzer now continues down through the operating supervision to the operator's level. It is explained to the operator what the analyzer is calculated to do for him in helping him supervise and operate his units more efficiently. Before he ever sees the analyzer installed, he becomes interested and is waiting to try and use it. In fact, in a good selling job he is as anxious to begin using the results as management is to see him do so. Simultaneously, we are working with the control laboratory personnel to acquaint them with the problems that we are going to experience in the initial calibration of the analyzer and with the fact that the results from the analyzer and the laboratory are not always going to agree.

During the engineering of the sample systems and installation drawings, the analyzer people who are going to be responsible for maintaining the analyzer are brought in. This gives them the background information they need to start their training program. The analyzer specialist is sent to the manufacturer's plant when the equipment is in the final stages of manufacture and calibration. The "debugging" and final calibration phase is a good time for him to learn most about the analyzer. Now we have everyone concerned familiar with the next analyzer installation.

We go through this procedure with every installation, and we think it is beneficial because we are able to go from the evaluation program release to the final use of the analyzer much faster than before this procedure was put into effect.

Equipment Selection

It is not quite so easy to select the wrong analyzer equipment now as it once was, but it is still much easier than selecting the right continuous analyzer equipment. We are constantly evaluating the knowledge and experience of the various manufacturers and users throughout the country. A final selection is made on the basis of the following items listed in the order of their relative importance: (1) applicability of equipment to our problem; (2) quality of design and workmanship; (3) experience and knowledge of the supplier; (4) service available (engineering and parts); and (5) price and delivery.

By using this basic approach, we have been able to obtain analyzers that do a satisfactory job. It now remains for us to do our part of the job.

Installation of Analyzers

The installation has to be carefully engineered from the point in the line where a sample is to be taken to the final read-out. The sample system will make or break a continuous analyzer installation and, like everyone else, we have had our share of troubles with sample handling. A good sample system must: (1) take a representative sample from the process where the process lags are at a minimum; (2) have the least possible time lag from the process to the analyzer; (3) provide proper filtering for removal of all contaminates that would interfere with correct analyzer operation; (4) present the sample to the analyzer at the correct pressure, temperature, flow, and phase; (5) dispose of sample after leaving analyzer; and (6) provide means for introducing calibration sample.

By satisfying all the points listed above, we now have only routine problems with sampling.

The primary device of the analyzer loop is installed in a housing designed for it. Installing the analyzer in a temperature-controlled building eliminates undue demands on the analyzer, sample systems, and personnel. In addition, our analyzer houses assist in fast, accurate calibration and repair as well as provide maximum security to the analytical equipment. In fact, our analyzer houses are accessible only to a relatively few authorized people. The cost of the houses usually is a very insignificant part of the total installed cost of the equipment. It has been one of the major factors, we feel, in keeping the analyzers in continuous operation (FIGURES 1 and 2).

Calibration and Performance Test

Any analyzer, regardless of how good or how well installed it may be, must be proved and must be correlated with laboratory results.

When the original problems are eliminated from a new installation, so that the analyzer operates continuously, we run an acceptance test in conjunction with our control laboratory. The acceptance test for a depropanizer, overhead chromatograph is a good example. All laboratory tests were run by the same man. The unit was under constant operation for the first six hours of the test. The unit operation was changing during the last three hours of the test. This shows up well on the curves plotted from our acceptance test (FIGURE 3).

FIGURE 1.

Figure 4 shows the calibration and correlation of another depropanizer, overhead chromatograph with the control laboratory. The laboratory variations have been attributed to sampling difficulties and the human factor in running the test.

The analyzers are checked periodically for calibration. This is done by using a standard sample with a certified analysis.

Figure 2.

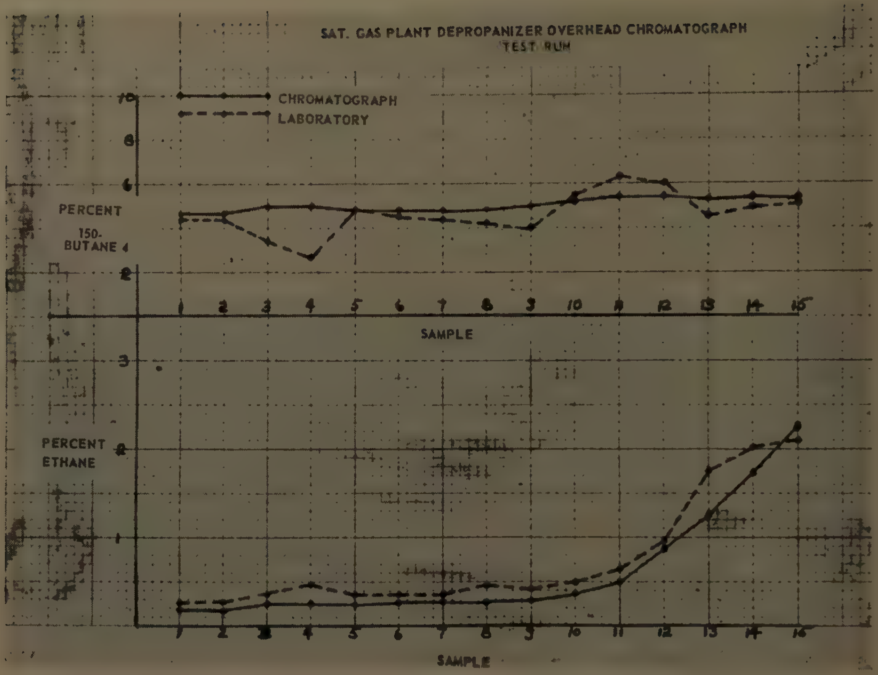

FIGURE 3. Saturate gas plant depropanizer, overhead chromatograph, test run.

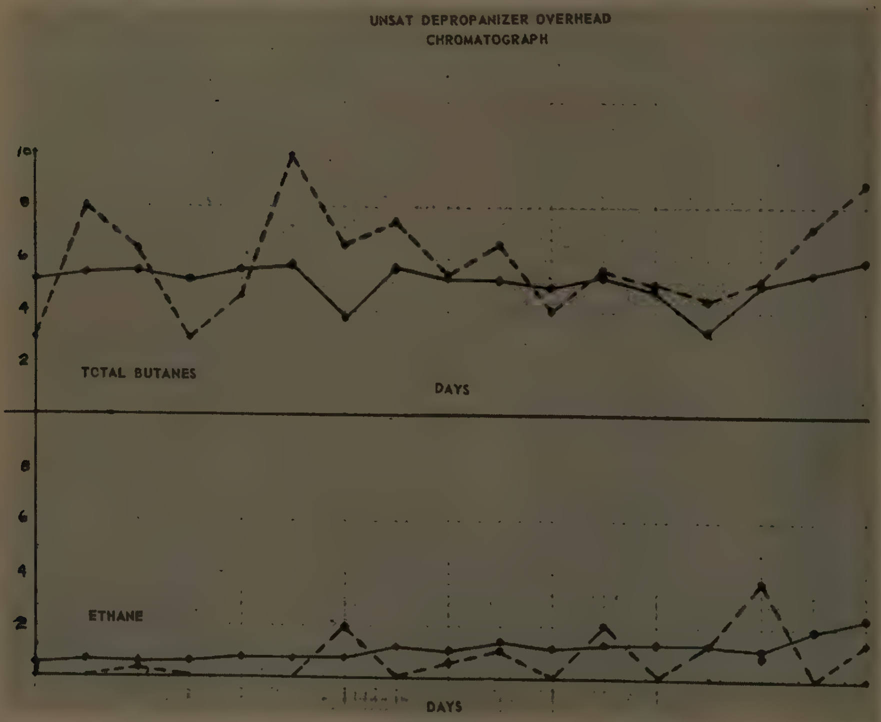

FIGURE 4. Unsaturate depropanizer, overhead chromatograph.

Analyzer Maintenance

After proper selection, installation, and calibration of our analyzers, we still have a qualified instrument man look over the analyzer systems once a day.

In this routine system check, a trained man turns up many minor items that need attention. These items are corrected before troubles are experienced with the analyzer. With trained men giving daily attention to the analyzers, problems can be immediately detected and solved. This is absolutely necessary if we are able to keep our analyzers in continuous operation. When troubles other than those of a routine nature are found, there is an immediate concentration of effort on the problem by our analyzer specialist and other analyzer-trained instrument men.

By keeping accurate records of the cost of maintenance per installation, we are able to reflect this maintenance cost in future justifications of this type of equipment. We find the average material and labor cost for each analyzer installation is approximately $1000 per instrument per year. In other words, an average of 200 man hours required per year per analyzer. This cost in man hours does not include the work done installing analyzers. The maintenance cost reflects the fact that even with this careful equipment selection, installation, calibration, and laboratory correlation, the analyzers still require routine maintenance attention to keep them in continuous operation. The success of the process stream analyzers still hinges on having a good qualified man, who is keenly interested in this type of equipment, looking after it continuously.

Based on our own experiences and those of others throughout the country, we have found that one qualified analyzer man is required for every 10 continuous process stream analyzers. A qualified analyzer man must: (1) be a highly competent instrument man; (2) have a basic knowledge of the chemistry involved; (3) have a good working knowledge of the process involved; (4) be able to work with and maintain electronic equipment; (5) understand the value of the analyzer to efficient plant operation, yet be capable and willing to take care of small routine details; and (6) have a thorough knowledge of the analyzers.

Men like this must be carefully selected, then given training in the areas where they are weak. This usually involves training in the theory of operation of the analyzers, in calibration techniques, in maintenance, in trouble shooting, and in the chemistry associated with the analyzers.

Operator Acceptance

With qualified manpower, day to day analyzer system troubles are immediately cleared up before they can interfere with the operation of the analyzer. The continuous, accurate operation thus made possible has been the biggest contributing factor in the acceptance of the process stream analyzers by our operating people.

No one can be expected to rely on or accept an instrument that is in and out of service or that cannot be expected to give reliable data. An operator wants to know more about what is going on in his areas in order that he may do his job better, more easily, and with more confidence. When he is convinced that an analyzer is accurate and reliable, he comes to depend on it for operating assistance. As we mentioned before, the education of the operating personnel on coming analyzer installations begins early in the engineering stages.

The operator has to be presented with data that are clear and in a form he can understand. He should not be called upon to make mental calculations on the data presented to him for operating assistance. A good example of this is chromatograph data. The usual presentation of process chromatograph data is in a form of a bar graph. Each bar represents a specific component in the sample stream with the bar height indicating the percentage of the component. Each group of bars represents an analysis. Unfortunately, this is not the type of data with which the operator is accustomed to work. He is more used to seeing data in the form of trends, such as that he sees on flow, pressure, and temperature records (FIGURE 5).

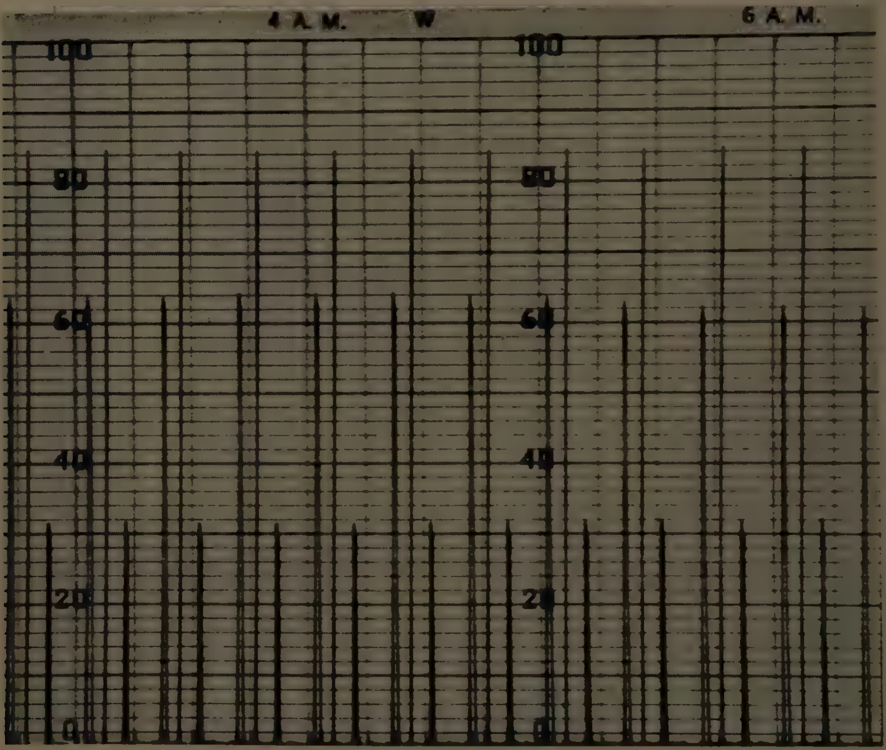

FIGURE 5. Chromatograph bar graph.

We chose to help the operator in this respect by recording each component on a separate pen on instruments similar to those he is accustomed to using with other process variables. Since the chromatograph is an impulse type of signal given at definite time intervals, we lock in the signal to each pneumatic-trend recording pen until a new signal comes in. Note the similarity to the analogue record that the operator reads and interprets on his other instruments (FIGURE 6).

In addition to better operator acceptance—when we have the equipment to produce a record such as this—the making of the analyzer system into a controller is a simple matter.

We feel that this type of equipment falls into two definite categories: (1) those intended for the assistance of operators and for future control of process units, and (2) those used by process engineers to study performance of operating process equipment.

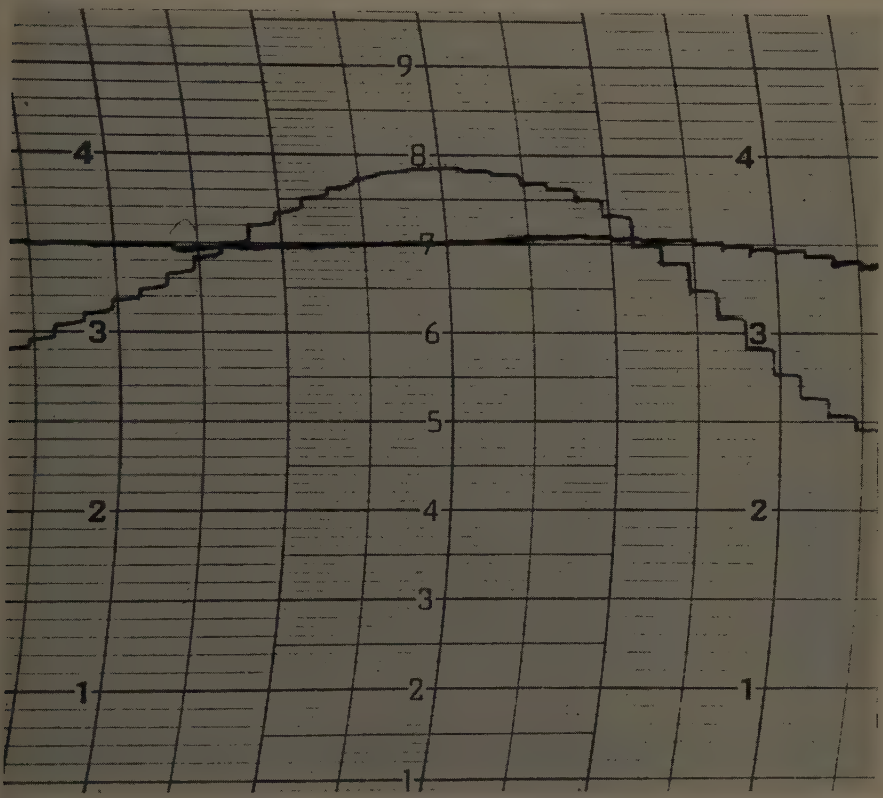

FIGURE 6. Chromatograph trend record.

In the first case, the instruments should be single-component, single-stream pieces of equipment with not more then two components per stream. In the second case, the equipment that the process engineers use to study process equipment can be the multiple-stream, multiple-component type of equipment since they can easily interpret the data presented from this type of equipment.

Analyzers as Control Devices

Control is a logical step from the point at which an analyzer is continuously and accurately monitoring a stream.

Whenever applying analyzers, an investigation should always be made to see if it is going to be possible to control with the device once it has been proved to give good, reliable, and accurate records. What we are actually striving to do is to control quality, not particular items such as temperature, flows, and pressures. An example of this follows.

In March 1960 we put into service at our Toledo refinery an end-point analyzer on the total Cat Distillate stream from our Cat Cracker Fractionator. After spending the usual amount of time in calibration and making correlations with the control laboratory, we had this instrument in continuous service for approximately six weeks drawing accurate and reliable records and being checked frequently by our control laboratory.

In May 1960, we put this end-point analyzer on control of the reflux to the Cat Cracker Fractionator. The end-point controller directly actuates the reflux-control valve instead of the more conventional method, that of resetting the temperature controller set point. While on temperature control, the top temperature of the fractionator was under good control, but the end point varied 10° or more and was erratic. A typical end-point chart with the fractionator reflux on end-point control shows the end point changing only ±1° or 2°. At the same time, the top temperature variation resulting from the end-point controller changing the reflux rate are rather minor (FIGURES 7–10).

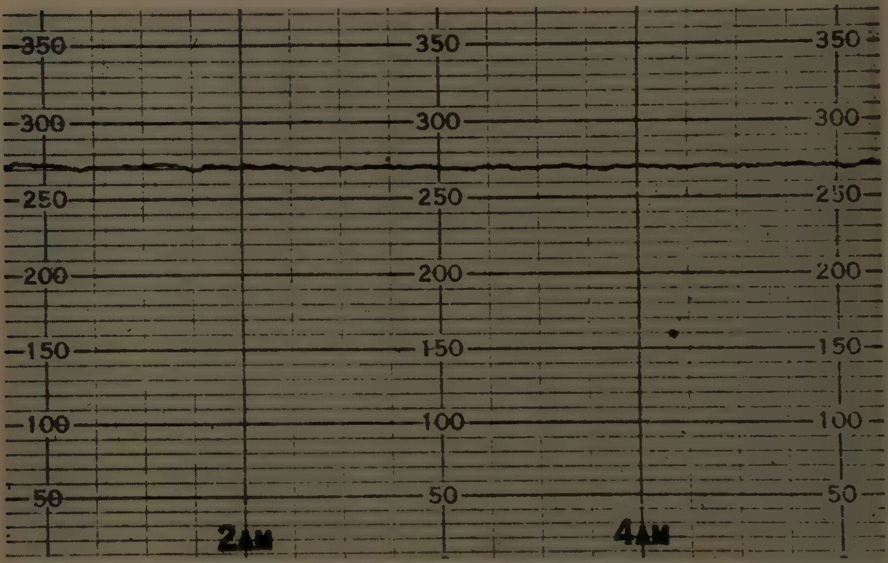

FIGURE 7. Fractionator on top-temperature control.

As predicted in our justification of the analyzer, we have been able to run 9° or 10° higher end point. This end-point controller returns approximately $40,000 per year.

This completely changes the operator's long-time concept of how to operate his units. As before, he always felt he had to have his primary variables—such as temperatures, pressures, flows, and levels—in the form of straight lines. However now we are telling him to permit the top-tower temperature to wander around and asking him to maintain control by the analyzer. Naturally this training of operating personnel does not take place overnight, and the operator does not give up his long years of operating experience after one or two installations of this type. However, after a period of watching the equipment in service he soon becomes aware that this is the correct way to control his units.

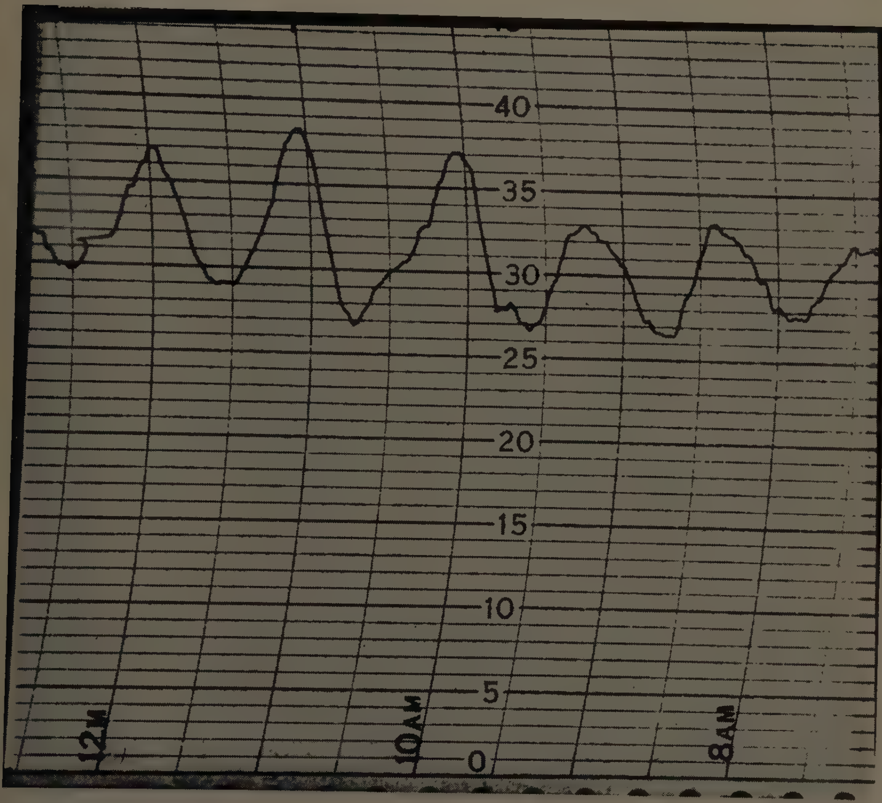

FIGURE 8. Fractionator end-point record with top-temperate control.

Other Analyzers

There is another whole group of analyzers that are very useful in plant operations but that are hard to justify economically. These are such things as dewpoint analyzers, combustibles analyzers, hardness analyzers and phenol analyzers.

Future Plant Analyzer Needs

We feel that we are just scratching the surface in the application of this type of equipment to our continuous processes.

Admittedly we have applied those analyzers commercially available that have proved accurate and reliable and have given results that we have been

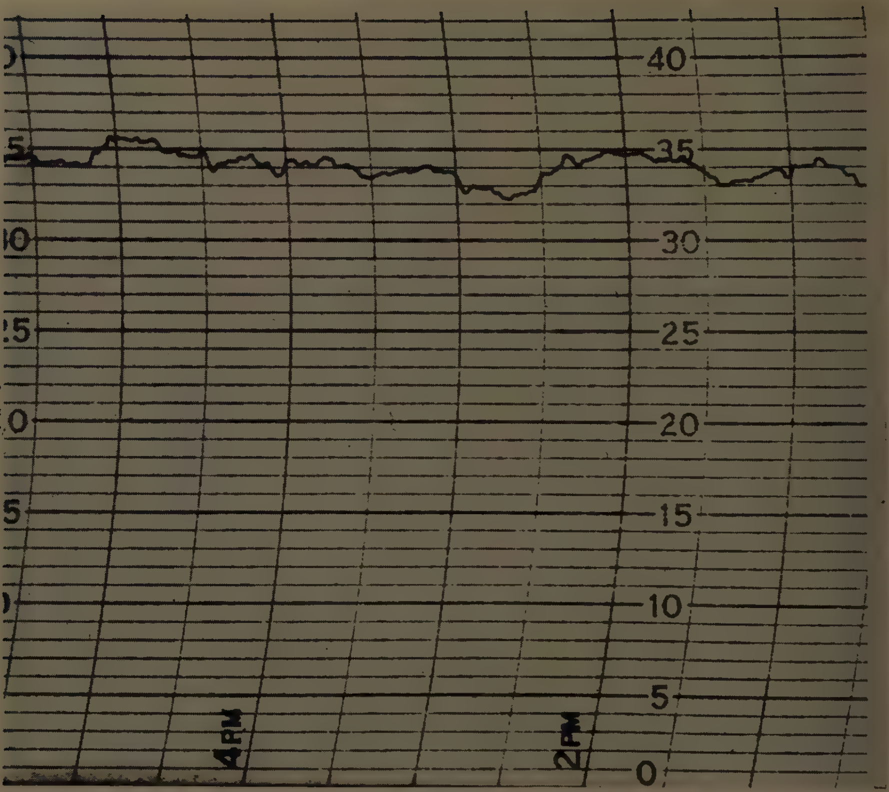

FIGURE 9.

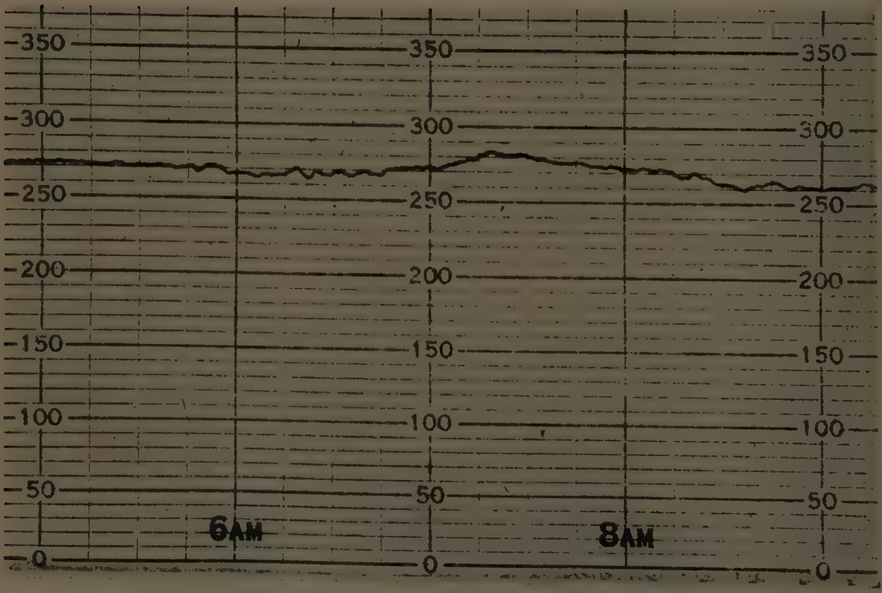

FIGURE 10. Top-temperature record with tower on end-point control.

able to interpret beneficially. There are many other quality measurements we should like to be able to make, such as continuous octane measurement, continuous freeze-point analysis, continuous per cent-off point machines, and odor machines. These are only a few. I am sure there are numerous others that, if they were available, we could easily start applying to economic advantage.

Conclusion

We feel that a complete analyzer program is the necessary step to reach computer control of our processing equipment. When we can accurately monitor all the quality measurements of our component and product streams, we shall know enough about our processing units, under all conditions, to be able to use computer control intelligently. We have found, under transient and upset conditions, that analyzers show us that we do not know what is actually happening in our units under all conditions. This equipment points out to us time and time again how little we know about process equipment that we have been operating for a number of years.

VISCOSITY MEASUREMENT AS USED FOR AUTOMATIC PROCESS MONITORING

Donald W. Brookfield and Richard A. Minard
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A Discussion of Viscosity

Viscosity is a product "dimension" instantly recognizable as such to anyone working with or looking at a fluid. Our good wives certainly must have an intuitive feeling for this property as they labor in the kitchen: indeed, examples of the most sophisticated type of viscous anomaly are to be found between the catsup bottle and baking pan. It has been only recently, however, that *continuous* measurement of this dimension has been employed as an analytical technique.

Let us quickly define viscosity, postponing for the moment a discussion of the techniques involved in its measurement and the various uses to which the resulting measurements may be put.

Although the world's first viscometer is found as a temperature-compensated water clock that dates back to 2500 B.C., the first formal attempt at analysis was performed by Isaac Newton in the early 1600s. He defined viscosity by considering the following model. Two parallel planes of liquid of area A are separated by a distance dx and move at a velocity differential dv. Newton assumed that the force F required to maintain this difference in speed was proportional to the velocity gradient dv/dx through the material.

Newton set up the equation:

$$\frac{F}{A} = \eta \times \frac{dv}{dx}.$$

Or this can be expressed:

$$\eta(\text{coef of vis}) = \frac{F}{A} \div \frac{dv}{dx}.$$

For this discussion, we can further reduce the defining formula to: the coefficient of viscosity is equal to the ratio of the shear stress per unit area to the rate of shear.

A material requiring a shear stress of 1 dyne/sq. cm. to produce a rate of shear of one inverse second has a viscosity of one poise or 100 centipoises. It is only by coincidence that water at room temperature has a viscosity of one centipoise.

By visualizing Newton's model of shearing lamina we can intuitively appreciate another rather broad definition of viscosity. It states this variable is "a measure of the rate of transfer of molecular momentum (in a simple fluid)."

There are a number of secondary variables that can serve to complicate the simple picture of viscous flow that has been presented. One factor to consider is that for any given liquid a change in temperature will cause an exponential change in its viscosity. This relationship will call for an accurate measurement of temperature if a subsequent viscosity measurement is to have any meaning. In process work this phenomena may call for the use of temperature-controlling equipment and/or a temperature-compensated viscometer; at best, viscosity measurement is essentially a two-dimensional proposition.

Another anomaly that must be fully appreciated in the purchase, use, or application of a viscometer is the matter of "non-Newtonian" flow. As previously stated, viscosity is defined as the shear-stress per unit area divided by the rate of shear produced in a fluid undergoing movement. Newton assumed that any change in movement (or shearing rate) would produce a corresponding change in the shear/stress with the result that the viscosity of a liquid would remain the same regardless of its rate of movement. A linear relationship between shear-stress and rate of shear was presumed. Such is indeed the case for a number of materials such as water, mercury, petroleum, some molten resins, and other such "simple" fluids.

Non-Newtonians do not behave in this fashion. A change in the shearing rate within a liquid will not cause an equivalent change in the shear stress. The viscosity, or resistance to flow, of such a liquid in movement, will depend upon the *rate* of movement. As a general rule most materials will "thin out" as they are being moved faster, although some slurries will thicken to the point of becoming solid, as the rate of movement is increased. Materials showing these effects have been categorized as pseudoplastic, plastic, or dilatant.

Another anomaly involves the dependence of a material's viscosity or resistance to flow: not only upon its rate of movement but on the time period that that movement has been in effect. As our wives might put it, "The longer you stir it, the thinner it gets."

These phenomena are so complicated, and yet so universal, that a whole new science has been established for the treatment of them called rheology. The name is taken from Greek and means "the science of flow." Rheologists somewhat facetiously claim that since "everything flows" theirs is a "science of everything." Facetious or not, when one is confronted by the seemingly infinite variety of materials that are the product of our modern economy, the utilization of which requires manipulation and control of their rheological behavior, he cannot help but feel the truth behind the humor.

There is, however, one ameliorating characteristic common to a considerable proportion of the foregoing materials, which can be termed "the consistency of the individual behavior patterns." This simply means that however complicated the flow-resistant properties of a product may be, the pattern and relationships are sufficiently stable that control of a single element or condition can maintain every aspect of its behavior. Therefore, although the technical rheologist must have in most instances extremely sophisticated instrumentation and employ complicated techniques to discover, evaluate, modify, and control the rheological behavior of his product, not so the actual production man. A relatively simple single-shear-rate continuous viscometer may provide excellent control. For example, lacquers, when acting as suspending media for metallic powders, usually exhibit peculiar flow properties. In use the extremely volatile solvents continuously evaporate, causing changes in all phases of the rheological behavior pattern. However, if the apparent viscosity at the point of measurement is restored by adding solvent, the entire pattern will be reestablished, and no change will be evident in the actual use of the lacquer.

However, just as it usually is necessary to determine viscosity at a temperature level consistent with the process, it may be equally requisite to measure the viscosity of anomalous fluids under shear conditions approximating those of subsequent processing. This will avoid placing undue reliance on the extrapolation of behavior patterns.

Nevertheless, the point cannot be emphasized too strongly that the rheological phenomena that I have just discussed must be thoroughly appreciated prior to: (1) establishment of any analytical procedure involving a viscosity measurement, (2) purchase, installation, and placement of a viscometer "in process," and (3) interpretation of results provided by an in-process viscometer. I in no way suggest that the measurements of even those materials exhibiting unpredictable rheological behavior is insurmountable. The measurement of such materials, however, places the instrument user in an area in which his own appreciation of the flow phenomena involved, coupled with the instrument manufacturer's "know how and experience," must be brought to bear.

All too frequently, however, both parties lack sufficient understanding of the rheological problems involved and of a given instrument's limitations in coping with these problems. This has apparently led to a very high percentage of misapplications in this particular field: higher, possibly, than in any other area of instrumentation.

Viscometric Methods

Let us now briefly discuss the various types of in-process viscometric methods upon which a variety of instruments are based at the present time. Unfortunately for my desire to appear completely objective, there are about as many different viscometers as methods. Each method is so distinctive that anyone having an interest in this field will immediately associate each principle discussed with a product name. Notwithstanding, I propose to plunge into an impartial analysis and, if at times it does not seem unbiased, I can only plead the dictates of judgement and experience. Our discussion will ignore the number of rather specialized instruments developed for particular materials and processes and therefore regarded as too specific in their design for general application. The methods presently honored by incorporation into equipment are: the vibrating element, the rotating element, and the piston (orifice). As a preliminary to analysis it might be well to note that there is no such thing as an ideal instrument. We may, however, list the features that such a hypothetically-ideal viscometer should possess to satisfy all requirements. Inasmuch as the particular needs of a potential user might require only a few of these features, it is possible that for a given installation even a generally inadequate viscosity in-process indicator could be considered a close approximation to the ideal.

The prospective users might do well to consider this list vis-a-vis their own applications in view of the complex nature of the materials, process conditions, and instrument requirements that may exist:

(1) The viscometer should be designed so that it can be universally and readily installed on existing process equipment.

(2) It should be capable of measuring materials over the complete range of process temperatures, pressures, flow rates, corrosive and vibrational conditions.

(3) It should be suitable for use in hazardous environments.

(4) The viscometer should be as free from cleaning requirements as possible. Sometimes during the run, but more frequently at the end of a batch or during a shutdown, many materials will harden, cake, or build up on the immersed portions of the instrument. Cleaning of those portions whose dimensions or mechanical performance determine the accuracy of the complete system should be straight forward and entail no likelihood of damage.

(5) Calibration should be permanent, and there should be neither short term or long range loss of standardization.

(6) The instrument's accuracy, repeatibility, and sensitivity should be better than demanded by the application.

(7) It should be durable and require a minimum of maintenance.

(8) The viscometer should be capable of modification to make its operating characteristics compatible with the type of material measured. Noncompliance with this requirement is a major reason for misapplication, and there have been numerous instances when excellent instrumentation has proved completely inadequate because the only variable it could measure was not the variable desired.

(9) To be ultimately ideal it should be able to delineate all aspects of rheological behavior. Actually at present there is no continuous in-process viscometer that pretends to evaluate even the simplest peculiarity of flow behavior, let alone cover every phase. This is indeed a drastic requirement since such a phenomenon, for example, as thixotropy involves a function of time. Thixotropy, of course, refers to the reversible process of building up and breaking down of structure in certain anomalous fluids that at rest form a solid gel whose viscosity appears infinite and, under shear, again becomes fluid. The time required for this transformation to take place can vary over wide limits, and its control can be exceedingly important. To illustrate, the modern paint technologist strives for very specific gel strengths and gelation rates in the formulation of his paints. If the rates are optimal, sufficient time for leveling will be allowed, and yet structure will be established soon enough to prevent sagging of the film. Nevertheless, however desirable, it is difficult even to conceive of a measurement of time-dependent variables on a *continuous* basis. In fact if conception of it were possible, gestation and delivery of appropriate instrumentation would undoubtedly follow in due course.

The first of the methods to be examined is based on the principle of the vibrating element that senses viscosity through the vibration of a magnetostrictive alloy. A thin strip of this metal can be made to oscillate by evenly spaced electrically induced pulses. The time required for this oscillation to dampen to a predetermined fraction of its original amplitude is measured. This measurement is reported in terms of the viscosity of the test material times its specific gravity. Measurements of this type are made with such rapidity that the instrument will indeed provide a truly continuous measurement.

In addition to continuous measurement, this type of instrumentation has a number of other advantages. Of all methods used, this presents the fewest problems in installation. The measuring element is small in size and nonsensitive to positioning; hence it may be installed in the side or even the bottom of the fluid container and requires only a threaded opening. Also, because of the small size of the element and, inasmuch as only that portion of the material forming a relatively thin coating on the surface effects the reading, but little sample is required. Since a tight seal into the process is provided, it does not interfere with vacuum or pressurized operations and is unaffected by these factors.

The method has certain inherent disadvantages, some of which are not too apparent to the rheologically uninitiated. The measurement is not solely in terms of viscosity but includes specific gravity. Continuous shear is not possible and whatever shear effects there are correspond to extremely high rates that, for reasons inherent to the measurement, cannot be brought down to usual process values. Because of the coating effect of the sample, undue lag in time may be experienced. The element is not particularly durable and can be susceptible to corrosion problems in active liquids.

This method lends itself generally to applications involving pure fluids and Newtonian flow, and its application to the measurement of such materials as slurries, suspensions and colloids is usually questionable: these require very careful study.

The second method of measurement in this analysis is the rotational, which measures viscosity by sensing the torque opposing the constant speed rotation of a cylindrical bob turning in the process material. Instrumentation based on this method reports its results in terms of the centipoise and will provide a truly continuous reading of this variable.

Additional advantages are that usual and predictable shear rates and shear effects are established. It may be used at any temperature for which a material may be obtained to make the bob. It senses the effect of shear on a gross sample and therefore is suitable for all kinds of fluids including nonhomogenous and multiphase mixtures as well as Newtonians. Immersed elements are rugged, and even severe mechanical cleaning does not impair operation or accuracy. Disadvantages of this method are that units must be installed vertically above the point of measurement; a certain amount of engineering may be required. The transmitting component usually requires limited purging. Adaptation to a pressurized system frequently presents problems and is not always feasible. Such a system requires more space than either of the other methods.

The third viscometric system, designated as piston-orifice, measures viscosity as a function of the time required for a weighted piston to sink into a sample-filled chamber against the resistance of the fluid as the movement forces it through the annular clearance between the piston and chamber wall. The time for each cycle is indicated on a chart and is a direct measure of viscosity. The particular advantages of this system are that it is extremely simple and that the principle of measurement has been widely used in manual instrumentation and is readily understood and related to practice. Again, it is easily installed and is small enough to permit wide latitude in choice of location. It is rugged and can stand abuse. Calibration does not drift.

There are certain disadvantages: foremost of which, if control is desired, is the intermittent nature of the indication. The inherent lag time is too great for many uses. It must be installed vertically. It is not suitable for use under pressure nor for high temperature. The piston can be immobilized by conglomerates, hence screening may be required and, with screening, clogging may be a difficulty.

In addition to these individual attributes there are several common to all three methods.

All instruments are suitable for operation under hazardous conditions.

All instruments provide wide rangeability but all the upper limitations in actual use are usually determined to a considerable extent by the feasibility of moving the sample to the sensing element without incurring excessive lag time. Of course, for processes in which changes in viscosity are followed that take place uniformly throughout the entire body of material, vibrational and rotational element systems suffer no such limitation, but piston-orifice type units here again experience possibly detrimental time lag because of the basic requirement that the sample must flow into and out of the measuring chamber.

All instruments are inherently sufficiently accurate, repeatable, and sensitive for the theoretical area of use to which each is individually suited. Gross inaccuracy, while frequent, is a result of misapplication, not instrument deficiency.

However, none of the commercially available instruments will completely satisfy the requirements outlined previously. The ultimate selection of an instrument will in many cases involve a compromise between what would be desirable and what is actually available. It is my opinion that continuous viscometry is still a considerable "art" and that the experience and advice (even if nearly smothered in sales effort) of as many instrument manufacturers as possible should be solicited. Even if the investment in the equipment itself does not seem to justify a wide investigation, the difference in effectiveness between the properly applied and the misapplied system of viscometry can be measured frequently in terms outstandingly important to the over-all economics of a given process.

A good part of the "art" referred to a moment ago must be employed in the actual installation of equipment. There are three primary ways in which all instruments are expected to be installed: in tanks that include storage vessels, reaction kettles, autoclaves, and blending vats; in pipe lines; and in sample chambers. The choice will depend on many factors such as the type of viscometric equipment involved whether the installation is in a process system or not, the particular location at which the viscosity need be known, and whether the sensing is to be used for indication or control. This last is most important. If for indication only, the sensing unit may be placed at any point the user desires and the type of instrument permits. Vibrational types as noted before are much less limited in this matter of location than either rotational or piston-orifice types, both of which must be vertical and above the liquid. However, if control is desired in addition to indication, and it usually is, the choice of location is no longer free; it is inextricably bound to and dictated by the parameters and characteristics of the process. It is at this point that the instrument engineer's knowledge, experience, and art should be enlisted to enhance the chances for success. Almost all failures of continuous in-process viscosity monitoring to provide acceptable control can be traced to either misapplication by using the wrong type of viscometric equipment or to lack of proper process control analysis. The engineer must interrelate all the factors affecting control such as flow patterns, lag times, means by which viscosity is maintained, rheological behavior, mixing, and pumping effects to specify not just the location of the viscometer, but very often modifications of the process itself.

Incidentally, various viscometric equipment based on the methods discussed will in general range in price between $1500 to $2000, depending of course upon the type of recording and indicating equipment desired. I am sure that there will be general agreement with the statement that the instrument's price, competitively speaking, should receive the least consideration in its selection.

The Need for Viscosity Control

In the previous two sections we have briefly defined viscosity and outlined the various means by which it may be measured in process. In several illustrative examples, we have noted the desirability of viscosity measurement with respect to specific materials and uses. Now the basic question of "why" will be discussed in more general terms.

I believe that the reasons for wishing to measure viscosity can perhaps be broken down to three primary groupings:

(1) A fluid's flow behavior can be a direct measurement of its "quality in service." Viscosity or, more directly, its flow behavior, will be a measure of its ability to be pumped, sprayed, or coated. If a power plant were burning Bunker C Fuel Oil, in-stream viscosity control of this material would insure uniform spraying characteristics at the nozzle and hence maximum combustion, efficiency, and power production.

(2) Viscosity is often a fundamental characteristic of a particular material. As previously mentioned, one definition of this variable is that it is a measurement of the transfer of molecular momentum. A change in viscosity therefore can reflect, in some cases, a change in the weight of the molecule itself. Indeed many in-laboratory measurements of molecular weight are made using very precise viscometers and applying a method originally outlined in theory by Albert Einstein. Viscometers are now mounted directly on reaction kettles to gauge the degree of polymerization of a resin in-process. In many cases, the "in-process" viscosity (at a known temperature) can be related to the change in molecular weight of a material.

(3) Viscosity can in many cases be related to other "hard to measure" variables such as solids content, crystal concentration, and specific gravity.

I know of one specific instance where an unusually shaped sensing element used in a rotational instrument gave effective indication of the type of crystal, whether needle or plate, precipitated from a process solution.

In many cases the application of an in-process viscometer must be preceded by a considerable amount of laboratory work before its need can be established. Conversely, there are many applications in which the need for a suitable instrument is known but cannot be filled. Nylon during the extrusion process might be a good example.

The advantages of continuous viscosity control are generally first realized in terms of greater product uniformity and quality. It has been my experience that in many cases the economic gains incurred, while considerable, often require rather close analysis to be traced. It has again been my experience that most users of this equipment are reluctant to disclose, for publication at least, the savings noted. In fact it is probable that the reluctance to publish is in direct proportion to the extent of the saving involved since such savings are a distinct factor in gaining a competitive edge. (As an extraneous remark, I would like to plead for a greater exchange of information between user and supplier in matters of this nature. I am sure that this would ultimately result in benefits throughout the industries involved and eliminate considerable duplication of development work.)

I shall cite two or three examples of a viscometer's application in continuous process work. The examples that will be discussed will illustrate the number of factors that must be considered in the design and application of this type of equipment.

Illustrative Applications

In the manufacture of Portland Cement, limestone and/or shale is ground in the presence of water in a ball mill, the feeds to which are continuous. From this mill the resulting rock-water suspension is passed through a classifier that removes the large rock residue held in suspension and returns it to the mill for regrinding. The material passed on by the classifier resembles a thick mud that in appearance and flow properties is quite similar to a neat cement paste. The mud is then pumped to a kiln where it is fired and from which it emerges in the form of a clinker.

Ideally, the output from the mill-classifier system should contain as much ground rock and as little water as possible, since an excess of water will reduce the efficiency of the kiln by requiring an excess of heat to drive it off. Another limitation to this process is that sufficient water must be present in the suspension to permit satisfactory pumping from the classifier to the kiln. Since the viscosity of such a suspension will vary markedly with the amount of water present, an in-process viscosity measurement will indicate its possibility for pumping and, indirectly, its water content. Viscosity control at an optimum point will insure efficient delivery of optimum product to the kiln.

Suspensions of this character are non-Newtonian in nature and, as such, must be measured at a constant rate of shear by an instrument capable of sensing its apparent viscosity, that is, the instrument should operate over a sufficiently gross sample to be affected by the presence of the rock particles or the addition of water.

A viscometric installation in the process described above has been made. A viscometer, placed between the classifier and the kiln, is now used to report the viscosity of the cement paste. After a period of several months in observing pump and kiln performance, an optimum viscosity as reported by the instrument was determined (I must point out that it took several months of rather careful study to arrive at this point, in view of the time lags and tremendous number of other process variables existing). After this value had been determined, an attempt was made to regulate the viscosity of the suspension through the controlled addition of water directly into the ball mill. It was found (again after several months of study) that the time lag and inadequate mixing within the mill caused a cycling of the viscosity output always in excess of the optimum value. A pneumatically actuated control valve was then placed to admit a trimming amount of water to the suspension directly at the pump bringing material through the viscometer and to the kiln. Placement of the valve at the pump insured thorough mixing of the water with the thick suspension and the production of a truly uniform viscosity output.

It is not expected that final data on improved kiln performance will be known for some time, although the consequences of such control would indicate that the savings involved will be truly remarkable.

It might seem that the application just discussed might be more reasonably solved by measurement of total solids or specific gravity. Such is not the case. Extremely small changes in specific gravity through the addition of water to a suspension will cause extreme changes in viscosity, the latter variable being the truly critical one. Study also disclosed that changes in the relative amount of limestone and shale used would affect viscosity while in no way affecting the specific gravity or total solids. To the best of my knowledge, analytical equipment of this nature is not usually found in a cement mill. The means of arriving at improved kiln performance are possibly more devious than a large number of instrument applications: it is hoped that this accounting will illustrate some of the thought, patience, and experience required in some instances in applying an analytical instrument.

Due to the relatively late arrival of usable process viscometers upon the scene, many processes exist that by reason of tradition and previous usage do not employ viscometers despite the basic nature of the measurement. Instead the attempt is made to control all possible variables that can conceivably affect the final result desired, which is the product's viscosity. Ingredients are specified with lower and closer tolerances in composition. They are weighed or measured with painstaking accuracy, mixed with extreme care, and processed under rigidly controlled conditions of temperature, pressure, agitation, and duration. Despite all this expensive, intricate, and time-consuming effort, the resulting viscosity may vary beyond acceptable limits and is rarely optimum.

Polymerization, asphalt blowing, and starch cooking sometimes fall within this category. Perhaps others in the field will agree that it is often difficult to introduce a direct analytical instrument into such an area where the large investment in time, effort, and money may produce a defensive reaction even when in possession of convincing facts and figures.

One application will be discussed in considerable detail. In it secondary instruments have been used, although not from choice. This has been in the manufacture of glass. To make a glass thread, hot molten material flows through a nozzle and is then immediately cooled. The rate at which the molten glass flows through the nozzle is a direct function of its viscosity. The ability of the glass to flow will of course determine the speed and effectiveness of the entire operation. In the manufacture of glass bottles the viscosity of molten glass and its resistance to shear will determine its ability to be formed and handled efficiently on production equipment. The in-process measurement of molten-glass viscosity has long been recognized as desirable: only recently has equipment been successfully applied.

The viscosity of glass in process is extremely high, being in the order of 1,000,000 cps. Like that of virtually any other fluid the viscosity will change with temperature. Common practice has been to measure and control very carefully the temperature of glass in process, it being recognized as the best way of regulating the flow characteristics of the material.

What are the problems involved in measuring the viscosity of molten glass? The temperatures are extremely high: in excess of 1800° F. The material is very corrosive and requires that any metal coming in contact with it be of a platinum-rhodium alloy. Due to its high viscosity some problems could also be anticipated in obtaining a representative sample. The equipment used in the manufacture of glass is run continuously for very long periods of time and does not permit shutdown except in isolated cases: it is necessary to install an instrument in an operating process with no opportunity of modifying the process flow.

The desirability of the in-process measurement of glass viscosity has been considered so great that some concerns in this field have devoted a considerable amount of development and engineering time to the problem. This work has not been in vain, and we can report that a number of instruments have been successfully installed. This has called for the use of a platinum-rhodium alloy spindle as well as for the shielding of the transducer from the extremely high temperatures found over the glass. The full results of this type of in-process measurement are as yet unknown. It has been demonstrated that the instrument may be used as a "fine tune" guide on the system's existing temperature controls. It had been presumed that the actual characteristics of the material in question would change very slowly with the hoped-for result that once an optimum operating viscosity (and subsequent temperature) had been established, the reading from such a viscometer would be referred to only intermittently. To the surprise of all concerned, it was discovered that changes in composition were found to be considerably more rapid and pronounced than hitherto expected, with the probable result that automatic control of the furnace temperature, based on an in-process viscosity measurement, will eventually be made.

The usefulness of an instrument in an application of this nature, while perhaps intuitively recognized, was rather difficult to pin down from a financial standpoint. This application has been discussed to illustrate the effect of viscosity on process performance and the steps by which this more direct analytical method is used at the present time to augment the existing instrumentation.

My experience has been that the use of a continuous viscometer has generally produced results that were in no way anticipated. It is generally an eye opener for people using this equipment to observe how much their product actually varies, due to unsuspected changes in process equipment, incoming raw materials, kettle cleanliness, and slight differences in operating techniques. Almost without exception the changes that are noticed are more gross and more frequent than had been expected. To generalize again, these effects are more pronounced in manufacturing processes using "natural products" that are either grown, mined, or pumped from the ground. Factors influencing the viscosity of tomato catsup include the amount of water and vinegar used in the cook-off and the processing equipment employed. However, also included is the chemical content of the tomato itself, which apparently varies with the type of vegetable, the soil in which it was grown, and the time of day at which it was picked (starch is also notorious in this respect).

In the application of a viscometer to any process, careful study of all the variables concerned should be made. In many cases it will develop that some factors are long-term or are not directly related to the ultimate objective of the control (the variations in viscosity with changes in limestone shale mixture in the application discussed is an example). In other cases, however, very careful analysis may eventually disclose that viscosity is not the answer.

The Shape of the Future

Now a word as to my estimate of the direction of future developments. It may be assumed that the various companies now producing in-process viscosity-monitoring equipment are continually laboring to improve their present products. Their principal efforts perhaps are to reduce or eliminate objectionable limitations, assuming such limitations are not inherent. They and perhaps others not now engaged in this field may of course develop still better instruments by using entirely different approaches in principle. Improvement can always be expected. However, the most interesting development may well occur in the area suggested previously by the statement that "a considerable proportion of rheologically complicated materials follow consistent behavior patterns once these have been established." Although it was noted that present equipment can deal with such products satisfactorily, how about the remainder whose behavior is erratic and for which control of the pattern itself is needed? This takes us into an area encompassing a great range of analytical sophistication. Instrumentation can be imagined as extracting a wide variety of items of rheological information and feeding these to a computer system for evaluation and calculation of necessary and controlling measures. Let us examine, for a moment, a hypothetical example: one that could be handled by present equipment without difficulty. We may imagine a certain compound formulated by the reaction (of several constituents) under controlled conditions. The rheological characteristics of this product are important but highly erratic, being greatly effected by minute variations in the purity of the raw materials. The particular property of interest is a propensity to exhibit shear-thinning which, it will be recalled, is a reduction in viscosity with increased rate of shear. Product performance requires a definite viscosity at a high-shear rate and an equally definite but substantially greater viscosity at low-shear rate. The various components have interrelated effects on not only viscosity levels but also on the specified ratio.

To meet this need a high and a low-shear viscometer could be used simultaneously to sense the values at appropriate shear levels and make this information available to a simple computer. The "brain" could then determine how to reproportion the composition to produce the ratio and values desired. To indicate how readily such control can be complicated, just consider adding even such nonrheological requirements as specific gravity and optimum cost control.

It can be stated without being unduly dogmatic that computer control of rheological behavior (beyond the present temperature compensation devices) will come. When it will come will depend on the potential value of automation becoming evident in this as it has in other areas.

Perhaps the most heartening feature as it relates to the instrument business as a whole is that present and potential investigators more and more often have the policies, personnel, and budgets available for explorations of this nature where the risks are known and the rewards are not clearly defined.

Part II.

AUTOMATIC PROCESS MONITORING BY UTILIZING ELECTRICAL PROPERTIES OF THE PROCESS MATERIAL

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Automatic Process Monitoring

As process technology moves steadily toward more extensive application of automatic control techniques, including computer control, the problems associated with sensing and determining both the qualitative and quantitative significance of process conditions are brought more sharply into focus. It would seem that the purposes of this monograph are to develop a clear concept of this total problem and to provide definitive information on applicable technology. This portion deals with measurement techniques that are well established and require no extensive presentation related neither to the basic principles of measurement involved nor to the details of available instrumentation. Accordingly, the purpose of this paper is to contribute perspective to the total picture by placing emphasis on the application significance of the various devices that fall within its scope.

In these days of rapidly expanding technology, a good deal of confusion sometimes arises from the terminology used. For the purpose of promoting a clearer mutual understanding, a few basic definitions are offered for consideration.

A *process* may be defined as an operation or combination of operations wherein input material (without particular regard for its form or degree of refinement) and processing aids are combined in proper sequence and under suitable conditions to produce one or more desired end products (output) at specified locations. By this definition a process may be a simple, single operation such as a differential distillation or an electroplating operation; or, on the other hand, it might be a highly complex combination of operations, as exemplified by continuous chemical processes such as petroleum refining or by an integrated electric power system involving a multiplicity of steam and electric generating units.

A *process material* may be considered as any material contained in the process stream at any point in the total over-all operation. A process material might be some form of the input material, a processing aid such as a solvent or a catalyst, or perhaps an intermediate reaction product occurring within the process that may have no ultimate value or use.

Since this entire monograph deals with automatic process monitoring, it seems pertinent to suggest that process monitoring includes all of the functions required to provide the necessary information and/or control relative to any portion of a total process. This total function therefore includes all of the sensing devices, transducers, controllers, and end operators such as valves, dampers, and pumps, as well as the devices required for computation, information display, data logging, and alarm signaling. The principal objectives of process monitoring may be summarized as follows:

(1) To optimize process efficiency (economy) while maximizing production of the desired end product by (a) maximizing the rates of the desired reactions; (b) inhibiting or minimizing undesired reactions; (c) assuring availability of process materials of desired quality in optimum quantities at the proper points; and (d) preventing loss of materials by spillage, leakage, evaporation, or other occurrences.

(2) To protect process equipment against damage by corrosion, excessive temperature, pressure, or other physical conditions, thereby minimizing maintenance and repair costs.

(3) To safeguard the public welfare by conforming to the prevailing requirements for industrial waste disposal, including air pollution and radiation hazard restrictions.

(4) To protect operating personnel and to insure over-all safe operation.

If it were not for the fact that in most processes the automatic monitoring requirements include relatively few devices that give specific information about the chemical composition of the input and output materials, there would be little need to have this paper published. The fact is, however, that the great bulk of information needed for process monitoring is not specific to determination of actual chemical composition of the input and output materials.

Monitoring Methods Based Upon Use of Electrical Properties

Automatic monitoring methods utilizing the electrical properties of process materials are not, in general, analytical methods of high specificity. Ordinarily they are not used to obtain precise information about chemical composition of a material. However, where the number of constituents in the process material is small and when qualitative composition is known, they can provide quite specific information. For example, the concentration of a particular electrolyte, when it is the only solute present in a solution, can be determined very precisely by a conductivity measurement. Moreover, there are many cases in which a specific electrical property of the process material or the desired end product is the characteristic of overriding importance and, in such a case, there is no more specific method than to measure the electrical property of particular interest.

The electrical methods discussed in this paper involve two general types of measurements; first, the measurement of potential difference and, second, the measurement of conductance or capacitance. Conductance and capacitance measurements are considered as one class since they in fact represent the same measurement techniques applied at opposite extremes of a binary measurement spectrum. One is seldom faced with the problem of measuring pure conductance or pure reactance in the measurements of significance in process monitoring, since the actual situation may be substantially removed from either extreme. Therefore, in both types of measurement, due regard must be given to the residual effects of the other property.

Potential measurements. In general, those potentials of interest in process monitoring are of the type classifiable as electrochemical-equilibrium potentials. The two most important applications, named in order of importance from the standpoint of extensiveness of use are: *p*H measurements and oxidation-reduction potential measurements. To a lesser degree the measurement of ion concentrations other than hydrogen or hydroxyl ions finds application in process monitoring. All of these measurements depend upon the existence of particular ions in a system.

The nature of these measurements is such that some comment about the importance of water is justified. Although water may be considered to be an insignificant component in the over-all constitution of the universe, it nevertheless is a compound of tremendous significance to the earth and its inhabitants. In considering all of the processes upon which our civilization is dependent, water is undoubtedly the preponderant process material. It challenges the imagination to think of a single process in which water, in one of its physical forms, is not involved either as a processing aid or as a component of the process stream. To cite an example of the importance of water: it is estimated that 1 billion tons of water per day move through the municipal water-supply systems of the United States, and substantially all of this is processed. To cite additional examples: it is estimated that it requires 1 ton of water to produce 1 lb. of refined sugar and that it takes from 20 to 50 gal. of water to put just 1 gal. of gasoline in a car.

One of the most unique and useful properties of water is its high dielectric constant (about 80), which is 3 to 4 times that of the alcohols and 15 to 20 times that of petroleum fractions. This particular property of water is important from the standpoint of promoting the ionization of electrolytes in accordance with Coulomb's law:

$$F(\text{force of attraction}) = \frac{Q^+Q^-}{ed^2}$$

where Q^+ and Q^- are the ion charges involved, d = distance between charge centers, and e = dielectric constant. It is obvious that the high dielectric constant of water operates to reduce the force of intramolecular attraction and, thereby, indirectly to promote ionization. This concept was originally proposed in 1923 by Debye and Hückel and its validity is supported by the much better agreement obtained between osmotic and conductance measurements, at least up to moderate concentrations, when dielectric constant of the solvent is taken into account.

Electrochemical potentials are related to ion concentration by some form of the Nernst equation. For example, pH (which is defined as $p\text{H} = -\log\,[\text{H}^+]$) is related to a potential by the equation:

$$E = E_0 - \left(\frac{RT}{F}\right) \log\,[H^+] = E_0 + \left(\frac{RT}{F}\right) (p\text{H})$$

Expressed more precisely in terms of hydrogen ion activity rather than concentration,

$$E = E_0 - \left(\frac{RT}{F}\right) \log\,({}^{a}H^+) = E_0 + \left(\frac{RT}{F}\right) (p^{a}\text{H}) \cdots \text{(half-cell potential)}$$

in which E is the potential of a "half-cell." Similarly, the oxidation-reduction potential of a generalized oxidation-reduction couple may be developed. For the equilibrium:

$$\mathrm{Red}^{xe} \leftrightarrows \mathrm{Ox}^{(x-n)e} + ne$$

$$E = E_0 + \frac{RT}{nF} \log \frac{[\mathrm{Ox}]}{[\mathrm{Red}]} \cdots \text{(half-cell potential)}$$

where Red = reductant, and Ox = oxidant.

There are a few important requirements worth emphasizing for making measurements based on these concepts. First, the potential relationships shown above are for half-cells. The half-cell itself must be of a type that responds, preferably, only to the ion equilibrium of interest; otherwise, mixed potentials are obtained. Obviously the half-cell must provide suitable means for external circuit connections. In addition, a second or reference half-cell is required to provide a complete cell whose potential may be measured. The reference half-cell, in addition to having suitable stability of potential, usually must be protected from the influence of the ions in the solution being measured. This is accomplished in most instances by use of a salt bridge. Since the salt bridge itself presents an interface with the solution under test, it must be properly designed to avoid, or minimize, the potential at this liquid junction.

It is common practice to refer to half-cells as electrodes or even as probes. The *p*H-responsive electrode in most common use today is the "glass" electrode which, because of its unique characteristics, does not respond to oxidation-reduction potentials. This makes possible the measurement of *p*H without interference from oxidation-reduction reactions, which is an important requirement in many cases. The so-called saturated calomel electrode and the saturated, or nearly saturated, potassium chloride salt bridge are the most commonly used reference electrode and salt bridge respectively. Potassium chloride is the ideal salt to use for bridge purposes: first because of its high solubility and high degree of ionization, which produces high ion density at the interface and, second because its two ions have very nearly equal mobilities. Other salts may be and are used in certain cases despite their less ideal solubility and ion-mobility characteristics as, for example, when the presence of chloride ions might cause undesirable precipitation of certain metal ions and complexes.

It is appropriate to emphasize the tremendous difference between the application problems characteristic of laboratory measurements and those of plant stream measurements. Special forms of apparatus are available to serve the needs of various field application problems. FIGURE 1 shows a flow-channel assembly made of cast plastic that is suitable for continuous flow applications where the discharge pressure is substantially atmospheric. The solution enters at the lower left-hand connection where it immediately comes in contact with the *p*H-sensitive portion of the *p*H electrode, continues its passage through the transverse channel making contact with the salt bridge surrounding the reference electrode, and passes finally through the right-hand vertical channel, which contains the resistance thermometer required for temperature compensation, to discharge from the upper right-hand port. FIGURE 2 shows a different form of flow channel, of cast metal construction, in which the solution enters through the bottom port and flows upward around the two electrodes and the temperature compensator and discharges near the top of the cylindrical section. The discharge port is not visible in this photograph, being located on the side away from the camera. This type of flow channel is used in low-pressure applications where it is desired to have a rugged system that can be supported directly by pipe connections. FIGURE 3 shows a form of assembly suitable for pipe-flange mounting in a pipe-tee. In this type, the flow of process fluid is at right angles to the vertical axis of the assembly, and correct orientation of the assembly is obtained by placing the glass electrode, which is on the left, in the

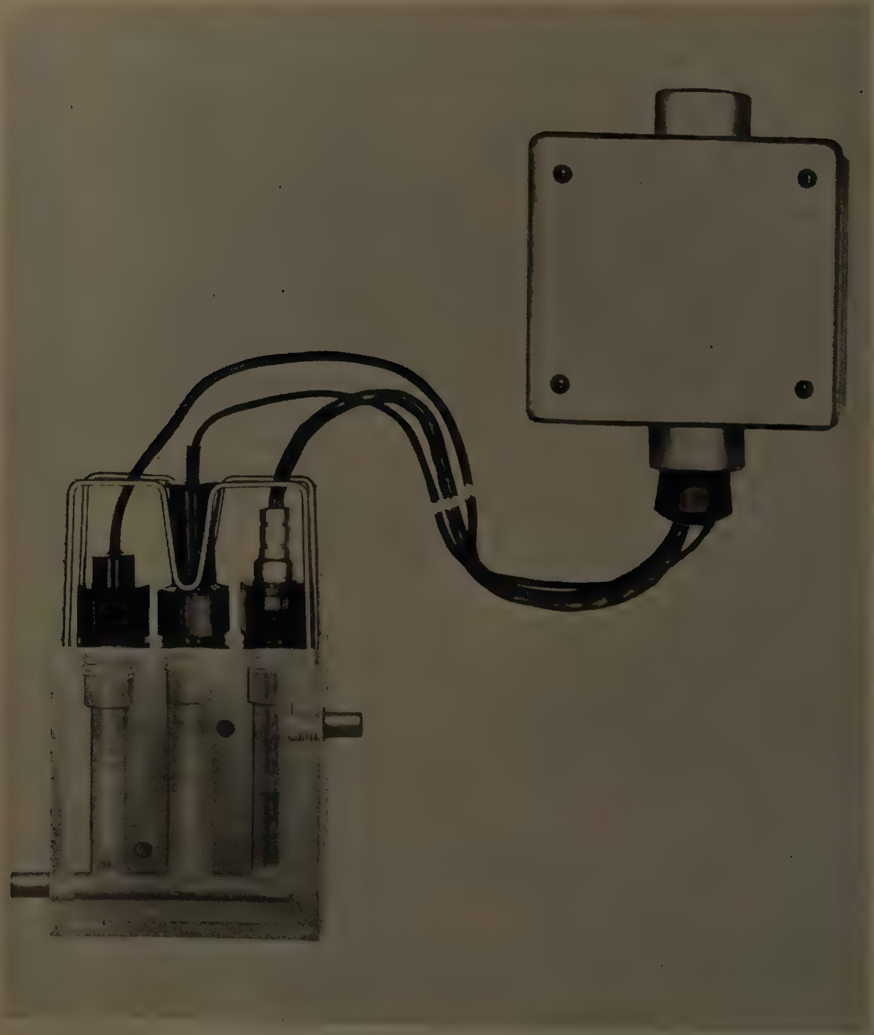


FIGURE 1. Assembly for measuring *p*H of flowing solutions.

upstream position. FIGURE 4 shows a dip-type assembly of electrodes that can be totally immersed in a vat or tank. A pipe of suitable length is threaded into the upper end of this assembly and the electrical connections are brought out through this pipe.

Conductance and capacitance measurements. In direct contrast to the potential measurements discussed up to this point, all of which are DC measure-

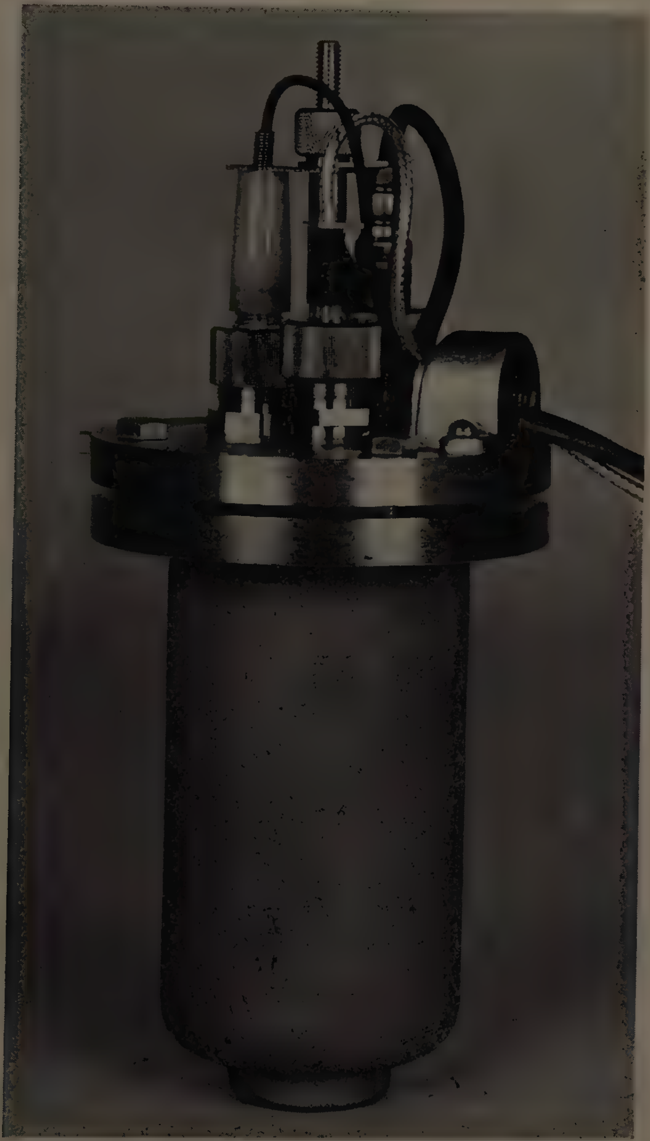


FIGURE 2. Assembly for measuring *p*H of flowing solutions.

ments, it should be noted that conductance and capacitance measurements are almost exclusively in the AC domain. In either conductance or capacitance measurements the sensing device essentially consists of two electrical conductors insulated from each other, both being exposed to the influence of the process material. There are two modes in which devices of this type are used, the most important of these being the situation in which the geometry of exposure of the two conductors is fixed. The only variable is that caused by changes in the electrical characteristics of the process material to which the

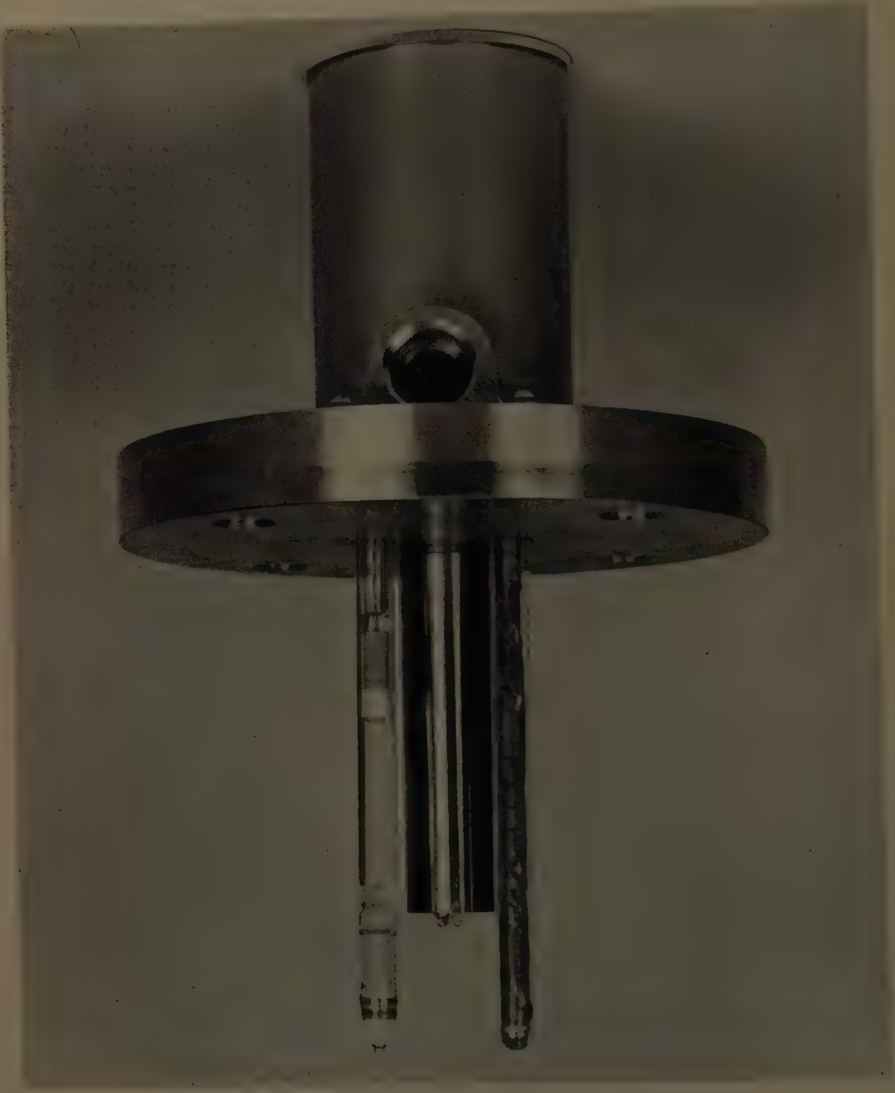


FIGURE 3. Assembly for measuring *p*H of flowing solutions.

two conductors are exposed. The second and less frequently encountered situation is represented by those cases in which the two conductors have a variable geometry of exposure determined by the process material as, for example, in level measurements. The latter mode of operation has the lower degree of specificity since there are two basic variables.

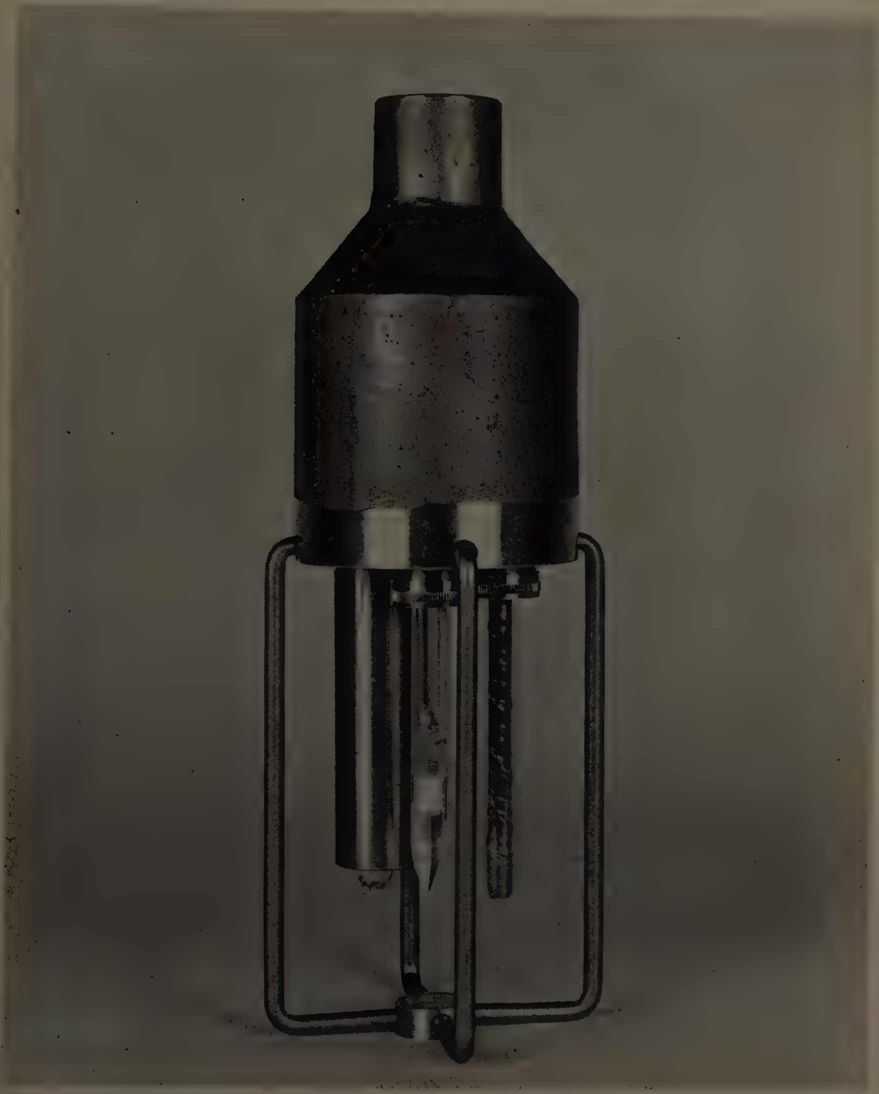


FIGURE 4. Dip-type assembly for *p*H measurements.

There are various forms of fixed and variable geometry systems useful in measuring the conductance or dielectric characteristics of process streams. FIGURE 5 shows 3 fixed-geometry configurations of electrolytic conductivity cells offering about a 50 to 1 range of cell constant. From left to right the cell constants would be about 0.02, 0.10, and 1.0 respectively. Cells of this type may be mounted in various ways for dip-type measurements or for continuous flow applications. FIGURE 6 shows another form of these cells that can be used to provide higher values of cell constant, from 10 to about 50. This type of cell has 2 vertical and parallel channels, in each of which is mounted a platinum ring. Such a configuration provides a long conducting path between the 2 electrodes and, consequently, the higher range of cell constant. Internal bore of the vertical channels and cell length are the 2 design variables that determine the cell constant. In FIGURE 7 is shown a form of conductivity cell suitable for pipe-line mounting through a gate valve.

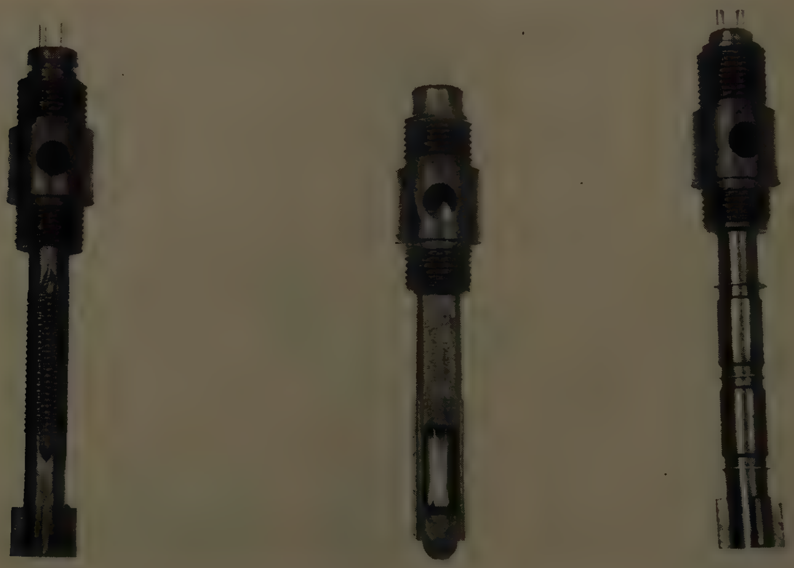


FIGURE 5. Electrolytic conductivity cells of moulded plastic construction.

It is well known, but worth emphasizing, that precise measurement of electrolytic conductivity requires minimizing of the effects of electrode polarization. This is accomplished first by applying alternating voltages to effect the measurement, thus avoiding polarization errors that would arise from the "plating out" of specific ions or the establishment of an ion-concentration gradient between the electrodes. The second measure usually taken is to platinize the electrodes by electrolytic deposition of a thin layer of spongy, platinum black onto each electrode surface. The platinum black serves principally as a catalyst for promoting the reversibility of ion reaction at the electrode/solution interface during reversals of the applied potential. The use of this procedure is not without its disadvantages inasmuch as platinum black has high adsorptive properties that can lead to errors, particularly when measurements are made in solutions of very low ion concentration. In general for solutions of high ion density, the platinizing procedure is essential but not very critical. On the other hand, for measurements in solutions of low ion density, a mere trace of platinum black (or sometimes none at all) leads to the most precise measurements. FIGURE 8 shows two hypothetical forms of fixed geometry systems suitable for capacitance measurements in pipelines. These might also be used for the measurement of moisture in fibrous and granular solids or similar materials by taking advantage of the increase in dielectric constant due to the presence of moisture.

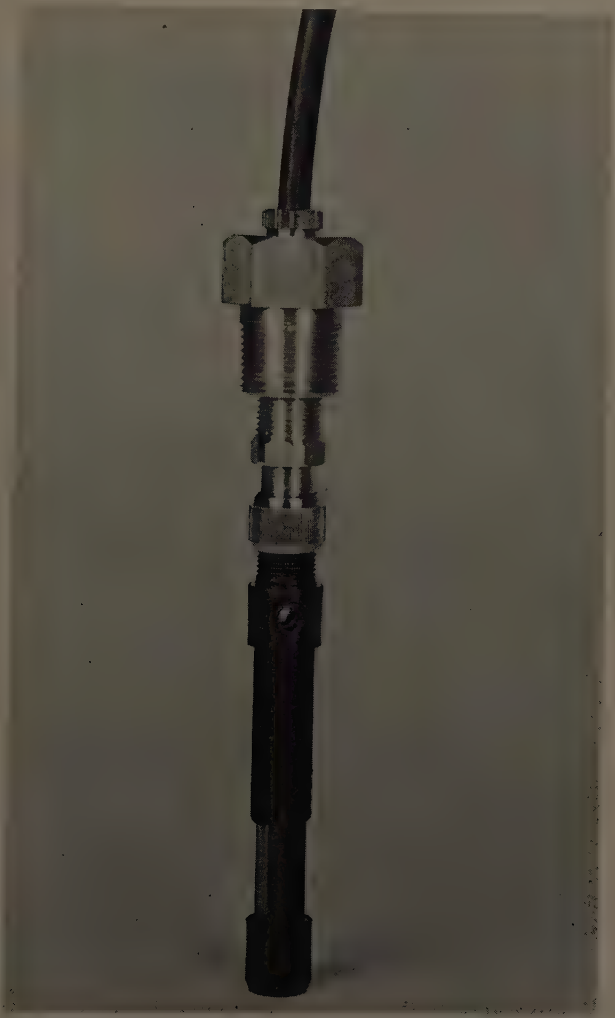


FIGURE 6. Electrolytic conductivity cell of high cell constant.

In FIGURE 9 an hypothetical structure is shown suitable for capacitance or conductance measurements based on variable geometry of exposure. This type of arrangement may be used for monitoring the level of process materials contained in tanks or vats.

There is still another form of measurement based upon the variation in capacitance between a probe and the process material or between two probes separated by layers of immiscible process fluids. In principle of operation,

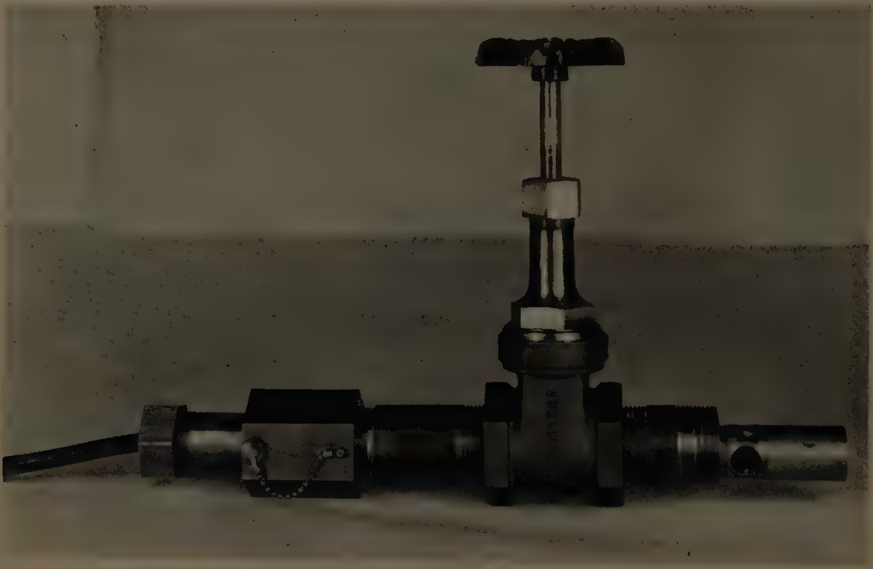


FIGURE 7. Electrolytic conductivity cell for pipeline mounting.

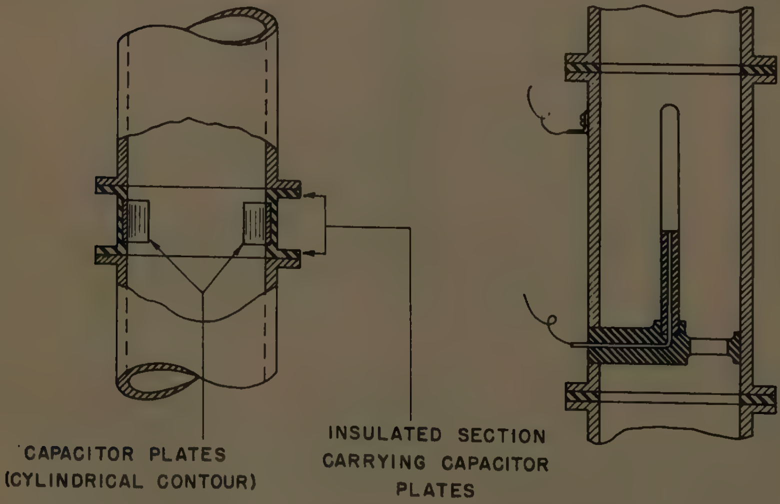
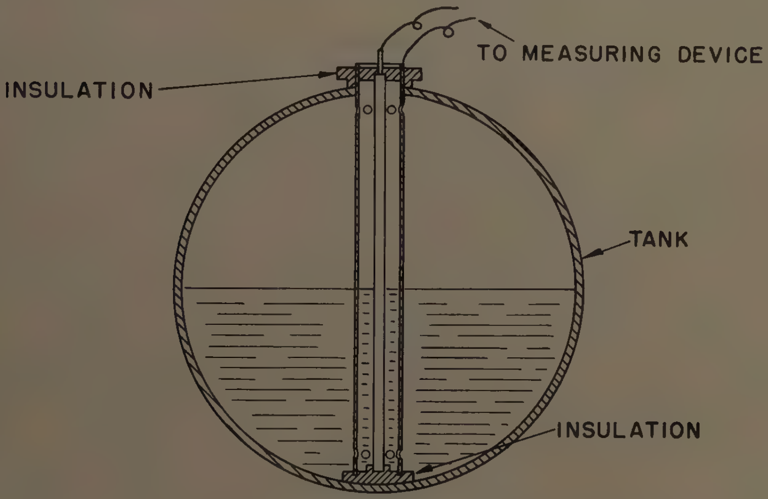

CAPACITOR PLATES (CYLINDRICAL CONTOUR)
INSULATED SECTION CARRYING CAPACITOR PLATES

FIGURE 8. Capacitance measurements in pipelines.

devices of this type make use of resonant-bridge controlled oscillators. The bridge contains inductance and capacitance elements, one of the capacitance elements being the probe and, at resonance, the bridge is in balance. Change in probe capacitance causes an unbalance output signal that may be used in various ways for process monitoring purposes.

Magnetic flowmeter. The magnetic flowmeter is a relatively new measurement tool applicable to fluids that possess conductive properties. For practical purposes, it has been stated[1] that the calibration of this type of device is unaffected by changing conductivity of the metered fluid when the conductivity of the fluid exceeds 200 micromhos (equivalent to about 100 ppm of salt in water). Operation of this device is based on Faraday's law of electromagnetic induction. As seen schematically in FIGURE 10, this device consists essentially of a section of pipe, a pair of electromagnets connected to be series-aiding and having a common axis perpendicular to the longitudinal axis of the pipe, and a pair of insulated contacts diametrically opposite each other and lying on an axis mutually perpendicular to those of the pipe and of the magnetic field. The contacts are insulated from the pipe but make contact with the fluid within the pipe. The pipe must be of nonmagnetic material, but preferably of metal to provide electrical shielding of the fluid. The interior surface of the pipe

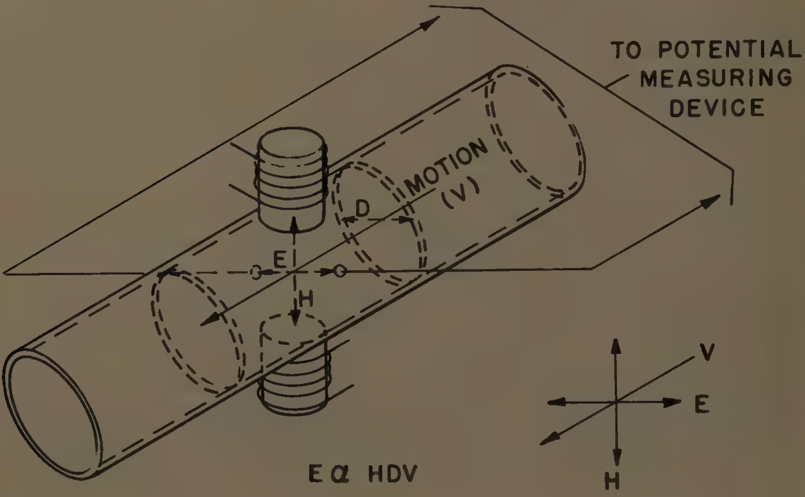


LIQUIDS: (A) CAPACITANCE MEASUREMENT FOR DIELECTRIC (NONCONDUCTING) LIQUIDS.
(B) CONDUCTANCE MEASUREMENT FOR CONDUCTING LIQUIDS.

ALTERNATE METHOD: (TANK MUST BE AN ELECTRICAL CONDUCTOR)
ELIMINATE OUTER ELECTRODE AND MEASURE FROM CENTRAL ELECTRODE TO TANK. THIS METHOD CAN BE USED FOR MEASURING LEVEL OF SLURRIES AND CERTAIN SOLIDS HAVING ADEQUATE "FLUIDITY."

FIGURE 9. Principle of level measurement (capacitance or conductance).

must be lined with a nonconducting material to prevent "short circuiting" of the induced potential. AC excitation is applied to the electromagnets, and the potential induced by virtue of the motion of the fluid will then be an alternating potential. The induced potential between the two contacts should be proportional to the product of the field strength (*H*) the distance between the two contacts (*D*), which usually is the inside diameter of the pipe, and the linear velocity (*V*) of the fluid within the pipe. *H* and *V* are the two parameters that can vary, but *H* can be made effectively constant by proper circuit techniques and/or control of the exciting voltage.



ELECTRODES MUST BE INSULATED FROM PIPE.
PIPE MUST BE OF NONMAGNETIC MATERIAL, PREFERABLY METAL (e.g. AUSTENITEC STAINLESS STEEL) TO PROVIDE ELECTRICAL SHIELDING OF THE FLUID.
INTERIOR OF PIPE MUST BE LINED WITH NONCONDUCTOR TO TO PREVENT "SHORT CIRCUITING" OF THE INDUCED POTENTIAL.
AC FIELD USED TO MINIMIZE POLARIZATION.

FIGURE 10. Principle of magnetic flowmeter.

By proper design, the magnetic field in the region of the two contacts can be made uniform. Thus the potential generated between the two contacts is proportional to average velocity and should not be affected by "velocity profile" due to viscosity or turbulent flow. Accordingly, flowmeters of this type measure the volume rate of flow at the existing temperature and pressure and are claimed to give results independent of viscosity, density, turbulence, or suspended matter. Flowmeters of this type have obvious advantages and are finding application where it is difficult to apply the conventional orifice-plate and venturi types of flowmeter. Applications of magnetic flowmeters have been reported for metering such fluids as corrosive acids, sewage, acid and water slurries, and paper pulp stock, as well as a variety of applications in the food- and beverage-processing industries.

Typical Applications

It will be obvious from the application examples now to be cited that electrical methods can be applied in meeting all of the principal objectives of process monitoring cited earlier.

Application to steam generators. Steam generators, particularly as used in the electric power industry, provide an excellent application example with which to initiate this portion of the discussion for a number of reasons:

(1) Steam generation represents a relatively simple and well-understood process.

(2) The input and output materials are water in different physical forms.

(3) Operating economy, especially in the electric power industry, is a very important factor. The process has been under critical study for many years, and process dynamics are relatively well understood by comparison to many other processes.

(4) Automatic process monitoring has been extensively applied, and without its benefit it would be virtually impossible to meet operating requirements.

In the water cycle there are four important points at which measurements based on electrical properties are made. These are:

(1) The *p*H of the boiler feedwater, which is usually maintained slightly alkaline to minimize corrosion and hydrogen embrittlement but not alkaline enough to cause foaming and priming in the boiler.

(2) Purity of the steam delivered from the boiler to the turbine, which is determined by measuring the conductivity of a condensed sample of steam withdrawn from the system; the purpose of this measurement is to determine whether particles of boiler water are being carried over with the steam; such particulate carry-over can have damaging consequences by eroding of the turbine blades.

(3) A conductivity measurement of the condensed steam after discharge from the turbine through the condensers and before return to the boiler feedwater loop.

(4) Conductivity, and sometimes *p*H measurement of the make-up water from the feedwater processing portion of the system.

Steam purity is one of the most critical measurements, and there are two systems commonly used for accomplishing this. In the Powell-McChesney[2] arrangement, a continuous sample of steam, taken directly from the steam header, is passed through a capillary tube whose length is calculated for the specified boiler pressure. This tube serves as an air-cooled condenser that partially condenses the steam. At the discharge end of the tube is a flow chamber containing a conductivity cell through which the condensate and uncondensed steam pass, the latter being exhausted to the atmosphere and carrying with it dissolved gases such as ammonia and carbon dioxide present in the steam. The condensate in the measuring chamber is in a state of high turbulence since the excess steam keeps the condensate at the boiling point regardless of ambient temperature. Maintaining the sample at boiling temperature prevents absorption of gases and, at the same time, eliminates the need for temperature compensation.

The second method for measuring condensate purity is that proposed by Larson and Lane,[3] and this method is preferred when volatile amines such as cyclohexylamine and morpholine are used in the boiler feedwater treatment. As in the Powell-McChesney system, steam is condensed at the atmospheric boiling point in a condensing chamber where carbon dioxide and other gases are removed by venting. The effluent from this chamber passes through a conductivity cell and upward through a hydrogen-ion-exchange-resin column in which the volatile amines, residual ammonia, and cations are removed and replaced by hydrogen ions. The condensate then passes through a reboil chamber that serves to decompose residual bicarbonates, bleed off the CO_2, and provide a sample at constant temperature for measurement in a second conductivity cell. The latter provides the important final measurement. The purpose of the first conductivity cell is to monitor the condition of the ion-exchange-resin column, since no significant difference between the two conductivity measurements indicates that the resin column requires regeneration. An additional benefit derived from the Larson-Lane method is much higher sensitivity since the cations present are replaced by hydrogen ions that have, roughly, about seven times the conductivity of metallic cations.

The foregoing somewhat detailed discussion of steam-purity monitoring serves to emphasize the requirements imposed by recent technological developments. The current use of steam generators operating at pressures near, or considerably in excess of, the critical pressure of the steam-water system imposes very stringent requirements for water and steam purity. In fact, the minutest traces of dissolved contaminants can have extremely deleterious effects. A comparable situation exists for water-cooled nuclear reactors and similar operations in which the water is exposed to high radiation fields. In applications such as these, monitoring of the efficacy of the water treatment system is of utmost importance, and great reliance is placed on electrolytic conductivity measurements for this purpose.

Additional electrolytic conductivity applications. In the paper-pulp industry the recovery of soda usually is economically justifiable. In this process, the so-called black liquor that contains the expended, as well as any excess, sodium hydroxide is drained from the pulp. The black liquor is the input material for the soda recovery portion of the process. In addition to the concentrated black liquor, the wash water used to cleanse the pulp also contains economically recoverable quantities of sodium salts, and some of this wash water also becomes part of the input to the recovery process. At some stage of dilution, recovery becomes noneconomic and conductivity measurements are used to determine the economic point at which wash water should be diverted from the recovery system and discharged as waste effluent.

In the field of municipal water treatment Knowlton[4] has reported on the use of a differential-conductivity measurement for controlling the fluoridation process and, later, Babcock and Knowlton[5] reported on conductivity-difference control of chemical coagulation.

In other industry areas conductivity measurements are used to monitor sulfuric acid concentration and nitric acid concentration in the production of these two acids, these being good examples of application of an electrical method for determination of quality of the output material. In the steel industry conductivity is used as one of the essential measurements for monitoring the condition of acid pickling liquors, in the rayon industry for monitoring the sodium hydroxide content of rayon spinning baths and, in the textile industry, for monitoring the alkaline mercerizing baths as well as the effectiveness of the acid neutralizing of mercerized yarns. In the wool processing industry the "carbonizing" operation is a dilute sulfuric acid treatment of the wool followed by neutralization with sodium carbonate, and conductivity measurement can be used for monitoring both steps of this operation.

*Additional p*H *measurement applications.* In addition to *p*H control of boiler feedwater already discussed in connection with steam generation for the electric power industry, other similar applications are found in process steam generators. In some process applications the make-up feed water is subjected to sodium and hydrogen-ion-exchange treatment. Treated water from the sodium units is alkaline, and that from the hydrogen units is acid. The two streams are then blended in a controlled ratio to yield a water of the desired *p*H value.

Throughout the process industries, cooling towers of wooden construction are used extensively, and the problem of protecting these against chemical and biological attack has been discussed by Conlan.[6] Chemical attack on the wood can be minimized by acid treatment of the circulating water to a value of about *p*H 6.5. Although *p*H control is effective in preventing chemical attack, it serves only to minimize the possibility of biological infection. Unfortunately, the microorganisms involved are quite tolerant to a wide variety of ambient conditions. It has been noted, however, that wood not under the influence of chemical attack is much more resistant to these organisms. FIGURE 11, which shows a dip-type *p*H electrode assembly exposed to a cooling tower effluent stream, is indicative of the type of application problem involved.

In the petroleum refining and petrochemical industries, *p*H monitoring is important in cooling tower applications just cited, as well as in *p*H control of dehydrator water for corrosion prevention, and in neutralization of acid sludge wastes, a pollution control problem.

It is well known that *p*H has an important influence on sedimentation rate and control of particle size in precipitation and crystallization processes. Examples of this type are found in the water treatment field and in the manufacture of pigments. In the latter case *p*H control also is important in reproduction of color specifications.

Examples of the use of *p*H control for optimizing the desired reaction and minimizing undesirable reactions will be of interest. In the first case a typical example is the application of *p*H control in the production of antibiotics. Both temperature and *p*H control are required to maintain optimum conditions for the growth of the organisms involved. This type of service imposes rather stringent application requirements on the electrode system since it must be capable of withstanding the required sterilization procedures. Another similar application is found in the fermentation process for production of citric acid.

An example of the use of *p*H control for inhibiting undesired reactions is found in the sugar refining industry, where the raw juice is treated with calcium hydroxide to precipitate carbonates and to adjust the *p*H to the optimum value for preventing inversion of sucrose. FIGURE 12 is indicative of the application conditions that have to be met in a sugar refinery.

FIGURE 11. Measurement *p*H of cooling tower effluent.

Still another important application of *p*H monitoring is found in the paper-making industry as shown in FIGURE 13. In this application the *p*H of the "white water" has an important bearing on the strength of the sheet, its color uniformity, life of the wire screen on the paper machine, and in the economic use of sizing chemicals.

FIGURE 12. Measurement *p*H in sugar refining.

One typical example in the waste treatment field is the acid-waste-neutralizing system at the New Jersey Zinc Company, New York, N.Y. FIGURE 14 shows a schematic of the process indicating the points of measurement and control.

One of the most recent applications of *p*H monitoring is in the refining of uranium ores. In this process, uranium ore is leached with sulfuric acid followed by resin adsorption of the uranium and then by a 3-stage precipitation

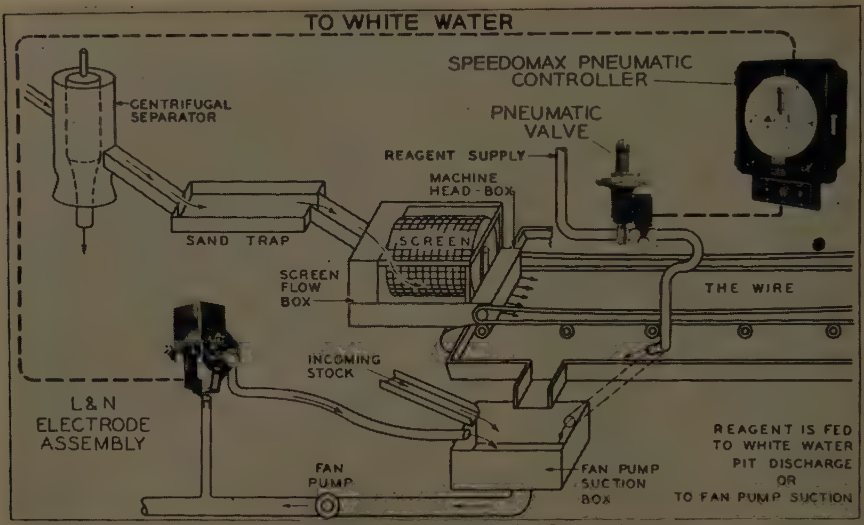


FIGURE 13. Schematic of *p*H control on paper machine.

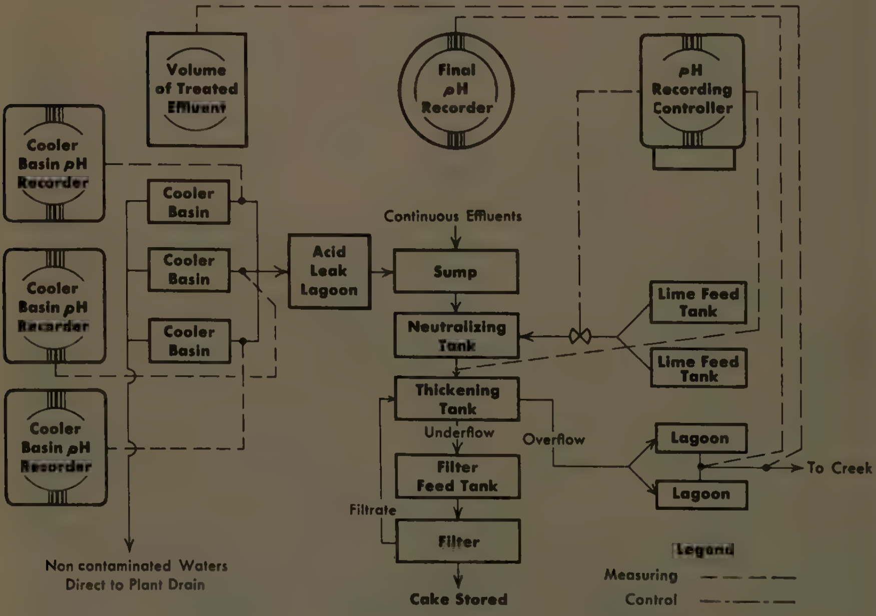


FIGURE 14. Schematic of waste treatment system.

and flocculation process. In the first stage *p*H is manually controlled at 3.6 by addition of anhydrous ammonia; in the second stage, which is similar to the first, *p*H is controlled at 4.8; in the final and most critical stage, *p*H is automatically controlled at 7.1 to produce the final slurry of refined uranium.

Oxidation-reduction applications. Oxidation-reduction, or redox, potential measurements are a relatively recent addition to process monitoring techniques and, thus far, they have been applied only to a limited extent. This type of measurement ordinarily cannot be considered as highly precise and specific, since industrial process streams often contain constituents, other than the one of interest, that can be involved in oxidation-reduction reactions. Nevertheless there are several significant applications of which a few typical examples are cited.

In redox measurements the active electrode usually is a piece of platinum foil or wire (with suitable connections to the external circuit) immersed in the solution under observation. As the ratio of oxidant to reductant changes in the solution, electron transfer occurs at the surface of this electrode. Almost all oxidation-reduction reactions involve hydrogen or hydroxyl ions. Thus changes in the net hydrogen-ion concentration also affect the potential of the electrode. Accordingly, almost without exception, it is necessary either to correct the redox potential for changes in *p*H or to control *p*H to a fixed value. As cited earlier, one of the outstanding advantages of the glass electrode for measuring *p*H is its insensitivity to redox potentials, and its use for *p*H measurements in oxidation-reduction systems assumes considerable importance.

Many dyes used in textile dyeing, such as indigo, are normally insoluble organic pigments that, when treated with alkaline reducing agents such as sodium bisulfite, yield a soluble compound adsorbable by the textile fibers. Subsequent air exposure of the fibers under suitable conditions reoxidizes the dyes to their original color and state of insolubility. The difficulty in practice is to produce and maintain the desired color shade on a continuous run of material. One of the most important factors in accomplishing this is to maintain the solution in the dyeing vat at a predetermined reducing power. This is accomplished by a redox measurement.

Another similar but more recent application is the copper dyeing of Orlon. In this process, cupric sulfate is partially reduced by a suitable reducing agent, such as hydroxylamine sulfate or sodium bisulfite. The ratio of cupric to cuprous ions, which can be determined by redox potential measurement, determines the color shade produced. In this continuous process the cuprous copper is taken up by the fiber and, under automatic redox control, a reducing agent is added to maintain the dyeing bath at the desired cupric:cuprous ratio.

Another and quite recent application of redox measurement in process monitoring has to do with the production of printed circuit boards extensively used for electronic circuitry. One operation in this process (this also is an important step in the making of copper photoengravings) is the etching of the copper laminate by ferric chloride solution. The rate of etching is critical because overetching weakens the bonding of the residual copper to the plastic supporting sheet. FIGURE 15 shows a continuous production line as used by the Radio Corporation of America, New York, N. Y., in the production of its

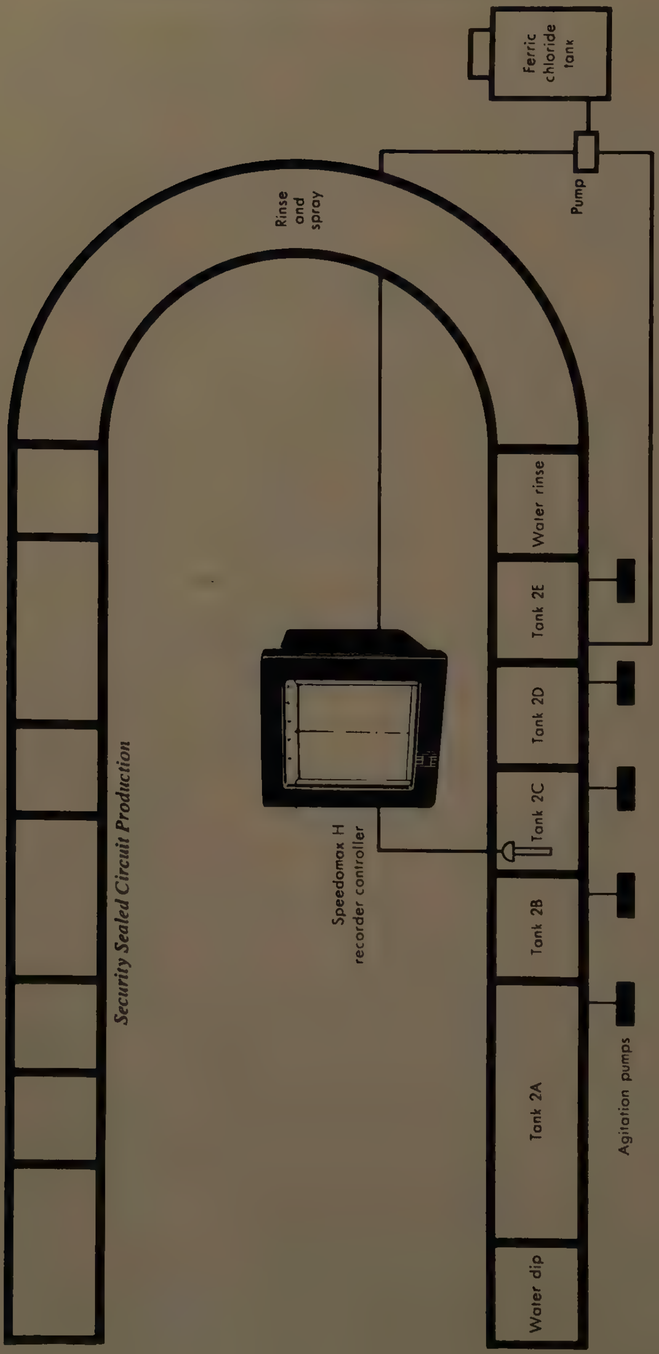


FIGURE 15. Schematic of redox control of copper etching.

"Security Sealed Circuits." This continuous system has 5 etching tanks in series, the ferric chloride solution being introduced in tank 2E and moving by successive overflows from one tank to another until it discharges from tank 2A. The flow of ferric chloride solution is counter to that of the work in process. The solutions in all of the etching tanks are maintained at 135° F. Optimum etching conditions are maintained by monitoring the redox potential in tank 2C.

The reduction of hexavalent chromium in chrome-plating wastes is one of several possible examples of the application of redox measurements as applied to waste-disposal problems. In this case the toxic hexavalent chromium is reduced, in an acid medium, to the relatively nontoxic trivalent form by reaction with reducing agents such as ferrous sulfate, sodium metabisulfite or sulfur dioxide. FIGURE 16 shows the schematic arrangement of an installation that handles the dual problem of disposing of both chromium wastes and cyanide wastes derived from plating and other metal processing operations. As shown in the left-hand portion of the figure, the acid and chromium wastes are treated with sodium metabisulfite in a reaction chamber under redox control. The right-hand portion of the figure shows the treatment of the alkaline and cyanide wastes by manually controlled chlorination. The two streams of treated waste material are then blended in a mixing tank where lime slurry is added under manual control. From the mixing tank the wastes go to a combined flocculation and settling tank. In this, lime slurry is added under automatic pH

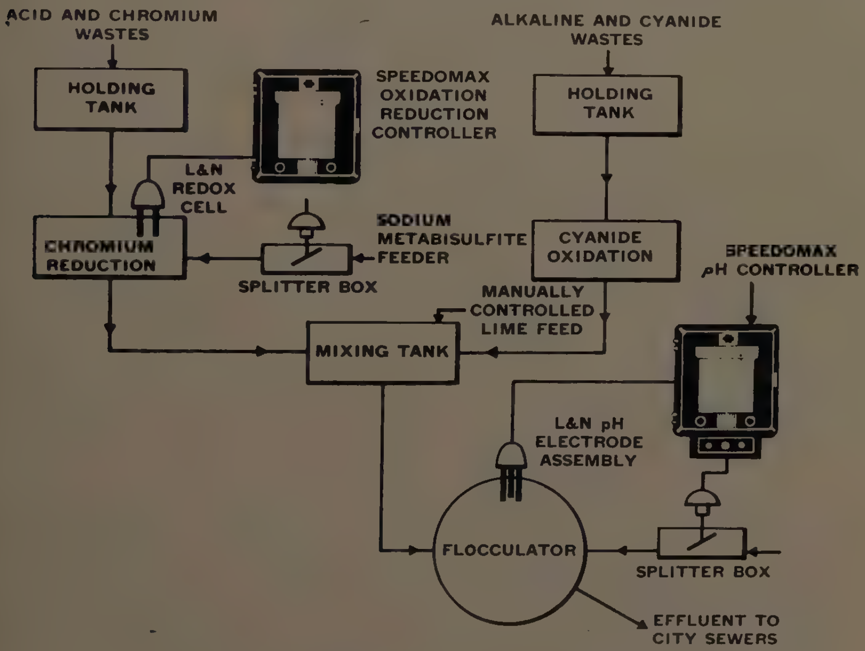


FIGURE 16. Schematic of system for treatment of chromium and cyanide wastes.

monitored control, to a final value of about *p*H 9 for precipitation of toxic metals as hydroxides. The supernatant fluid is then acceptable for discharge to the city sewer.

Present Situation and Future Prospects

The application of measurements that utilize the electrical properties of process materials has experienced a consistent growth through the years with no indication of leveling off. A major factor in this growth undoubtedly is the tremendous expansion of all activities associated with automatic process monitoring in existing as well as in new processes. As long as water continues to play the important role that it does as a processing aid and as a constituent of process streams, we may expect measurements based on electrical properties to continue to be an important element of the total process-monitoring function. Accordingly, the future for instrumentation of this type appears most promising.

Quite apart from the growth factor, there are significant indications of the need for applying measurements of this type under more and more difficult application conditions. Among important current trends are the use of higher temperatures and pressures, particularly in the power field, and the contemplated more widespread use of nuclear power for nonmilitary purposes. Still another important factor is the increasing demand for completely safe, as well as fail-safe, process operation with minimum disturbance in quantity and quality of output, preferably with no unscheduled down time.

It is apparent that instrument manufacturers and users, alike, may face the future for this type of instrumentation with confidence that unusual opportunities accompanied by unusual challenges are to be expected.

Acknowledgments

In a general paper of this type, the material is drawn from numerous sources and represents the work of many individuals. I am therefore indebted to several of my associates within the Leeds & Northrup Company for their technical contributions over the years and for specific assistance in providing material for this paper.

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THERMAL PROPERTIES AS USED FOR AUTOMATIC ANALYSIS

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Every chemical reaction and many physical processes involve a change of the thermal energy of the reacting system. It is therefore quite obvious that thermal properties can be utilized by the process industry for automatic continuous monitoring and analysis.

Measurement of Temperature

All measurements of thermal properties amount ultimately to a measurement of temperature. In the process industry the following methods are used chiefly for temperature measurements:

Differential expansion of solids. Devices based on the thermal expansion of solids consist of structures composed of bimetal elements in the form of strips or coils. Bimetallic elements are not as much used for measuring temperature directly as for control purposes. Their useful range is from −75 to +1000° C.

Thermal expansion of liquids. Thermometers using expansion of liquids, such as mercury, alcohol, and pentane, are well known. The range of thermometers containing liquids is from −90 to +550° C. (with compressed nitrogen above the mercury). A variety of bulb thermometers are available for continuous recording and controlling of temperature.

Resistance thermometers. Resistance thermometers are based on the change of electrical resistance of a wire element with temperature. The most reliable resistance thermometer is constructed of a platinum coil having a temperature coefficient of resistance of 0.003920 (min.). Platinum resistance thermometers can be used from −220 to +750° C. and are eminently suited for process applications. Preliminary work with high-temperature precision resistance thermometers using Fibro platinum* as the resistance element has shown great promise at temperatures approaching 1100° C.

Another type of resistance thermometers are thermistors[1a,b] composed of mixtures of certain semiconducting metal oxides such as the oxides of cobalt, copper, iron, magnesium, manganese, nickel, tin, titanium, uranium, and zinc. Thermistors are available for the range of −100 to +500° C. Mostly they are not used for measurement of temperature but for monitoring or controlling within a narrow temperature span, 1 to 2° C., the temperature coefficient of resistance of thermistors being much higher than that of metals; for example, for ($NiO + Mn_2O_3$) it is about -44×10^{-3} $(°K)^{-1}$ at 0° C. opposite in sign and more than 10 times as large as for platinum.

Thermocouples. Thermocouples are based on a principle discovered in 1821 by T. J. Seebeck that metals or alloys of different compositions in contact with each other develop an electromotive force in a temperature gradient. Thermocouples are available for a wide range of temperatures: tungsten versus rhenium-26, tungsten-74 alloy can be used up to 2800° C.; iridium versus tungsten up to 2100° C.; and the iridium versus iridium-rhodium series to 2000° C. For the region of 1400 to 1800° C. platinum-rhodium alloys of various composition can be used such as platinum, 6 per cent rhodium versus platinum 30 per cent rhodium. The platinum versus 10 per cent rhodium-90 per cent platinum couple is applicable for continuous operation up to 1400° C. Between -190 and $+1200$° C. the Chromel-Alumel* couple is suitable. For the upper region of this temperature range a palladium-gold versus platinum-palladium-gold couple named Platinel† has recently become available that offers superior stability and more corrosion resistance than the Chromel-Alumel couple. For lower temperatures iron versus constantan (-190 to $+750$° C.) and copper versus constantan (-190 to $+350$° C.) are adequate.

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* Registered trademark, Engelhard Industries, Inc., Newark, N.J. Br. P. 849,431.

Radiation pyrometry. Instruments based on measurement of emitted radiant energy are either radiation pyrometers or optical pyrometers.

Radiation pyrometers determine temperature by focussing the entire radiant energy from an object—light and heat radiation—on a sensitive thermopile. The temperature scale of radiation pyrometers is based on the Stefen-Boltzmann law that the radiant energy from a black body is proportional to the fourth power of its absolute temperature. Measurements with radiation pyrometers can be made beginning at 50° C. usually up to 1750° C.

Optical pyrometers are operated either photoelectrically or visually, the latter type being the official instrument for the International Temperature scale above the melting point of gold (1063° C.). In the visual optical pyrometers the emitted radiation of the object in a narrow spectral band of an average wave length of 0.65 μ is compared with the radiation from an energy standard. The temperature scale is based on Planck's or more commonly on Wien's energy distribution law. The optical pyrometers are, in general, between 750 and 3200° C. Special instruments have been constructed up to 5500° C.

Process Monitoring Utilizing Heats of Reaction

Continuous process monitoring and analysis based on measurement of reaction heats can be carried out either directly in the reacting system itself or indirectly on suitable sample streams. Wall[2] has pointed out that heat losses to the environment represent the factor most limiting control accuracy. Since, however, in many chemical processes the heat effects involved are large and since normally in such process streams heat capacities and densities do not vary significantly, conditions can be obtained where precision and reproducibility are high and, consequently, satisfactory process control is feasible. This can be realized both for thermal measurements in the reacting system itself and for measurements in sample streams.

Measurements directly in the process stream have the advantage of fastest possible response. Frequently it will not be possible to analyze a specific component by such measurements since a process may not necessarily yield only one or a given number of reaction products. However, for continuous monitoring and control it is often superfluous to have information on the individual reaction products. The measurement of the heat developed or absorbed by the process is sufficient to insure proper performance of the system. This may be illustrated by a few examples.

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* Registered trademark, Hoskins Manufacturing Co., Detroit, Mich.

† Registered trademark, Engelhard Industries, Inc., Newark, N. J. F. P. 1,244,569.

An illustration for essentially endothermic reactions is found in the petroleum industry's reforming process to upgrade naphtha of low octane rating into high octane gasoline by processing over a platinum catalyst. The chemical reactions taking place in this process are dehydrogenation of naphthenes to aromatics, isomerization of straight chain paraffins into branches paraffins, dehydrogenation and simultaneous isomerization of naphthenes into aromatics, dehydrocyclization of paraffins into aromatics, and hydrocracking. For each of these processes a typical reaction is cited in TABLE 1.

TABLE 1

C_6H_{12} (cyclohexane) → $C_6H_6 + 3H_2$	−55.3 kcal./mole at 500° C.
n-C_6H_{14} → iC_6H_{14}	−1.7 kcal./mole at 25° C.
C_6H_{12} (methylcyclopentane) → $C_6H_6 + 3H_2$	−45 kcal./mole at 25° C.
C_7H_{16} → C_7H_8 (toluene) + $4H_2$	−67 kcal./mole at 500° C.
$C_6H_{14} + H_2$ → $C_2H_6 + C_4H_{10}$	+11.7 kcal./mole at 500° C.

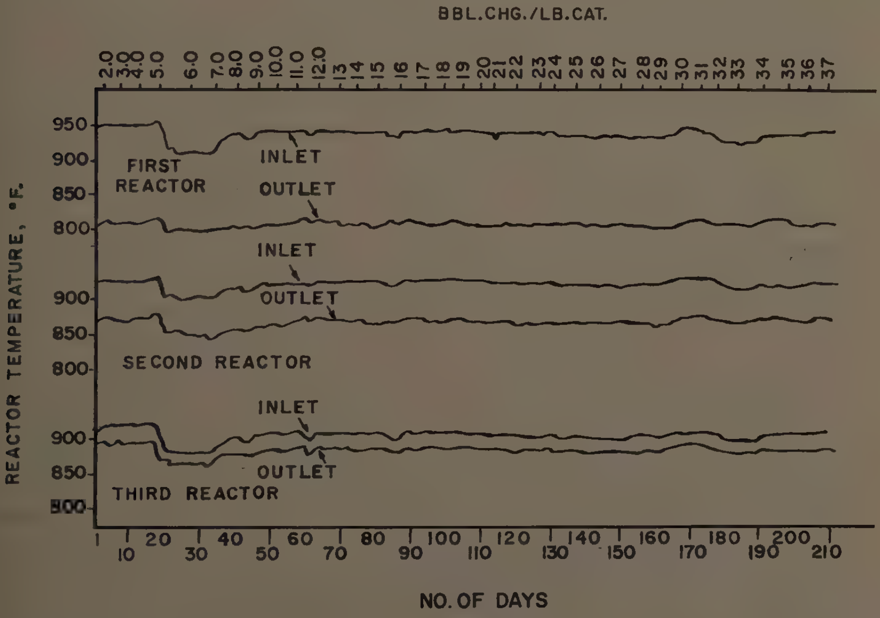

FIGURE 1. Monitoring of reactor performance in naphtha reforming by indication of endothermic reaction heat.

Except for the last reaction the reforming reactions are considerably endothermic. The process, therefore, is usually carried out industrially with at least three reactors containing the catalyst and having preheaters ahead of each reactor. Thermocouples are arranged throughout the reactors to measure the temperature of the entering gas and the temperature distribution throughout the catalyst bed. A typical temperature distribution in a series of three such reforming reactors is shown in FIGURE 1. It is seen that the temperature differential in the first reactor is about 130° F. and in the last reactor about 50° F., the decrease in temperature differential being indicative of completion of the reaction. The importance of monitoring these temperatures continuously lies in the fact that these temperature data supply immediate information on the proper functioning of the process. If the catalyst becomes poisoned or otherwise inoperative, its malfunctioning would be immediately indicated by the temperatures before this was found analytically or by measuring the octane rating of the product. Monitoring the temperatures, therefore, permits an immediate control and often immediate correction of the operation.

A case where direct measurements of reaction of an exothermic reaction heat are of interest is given by the oxidation of ammonia to produce nitric acid. The basic oxidation reaction is: $2NH_3 + 2.5O_2 \rightarrow 2NO + 3H_2O + 54.5$ kcal./M at 950° C., the nitric oxide formed being converted into nitric acid in subsequent steps. Nitric acid plants are usually operated in catalytic reactors containing layers of gauze, usually of platinum rhodium alloy with air:ammonia ratios to yield an effluent temperature of 900 to 950° C. usually at a pressure of the order of 6 to 7 atmospheres. The temperature in the reactor is measured by suitably arranged thermocouples. The temperature established in the reactor is strongly dependent on the ammonia:air ratio. In the event the ammonia:air ratio should, due to this operation, change, for example to an ammonia:oxygen ratio of 2:1.5 instead of 2:2.5, the process might change to the following: $2NH_3 + 1.5O_2 \rightarrow N_2 + 3H_2O + 92.5$ kcal./M at 25° C., yielding a theoretical reaction temperature of 1775° C. Obviously, neither the materials of construction of the reactor nor the catalyst could withstand such high temperatures. Indeed, the unit could be destroyed within a very short time. Consequently it is important to monitor the temperature continuously. Any sudden increase, which may be caused by an upset of the air:ammonia ratio, could be utilized for corrective measures. For instance, in a small nitric acid plant operated by Engelhard Industries, Inc. the reactor temperatures are fed to a controller that will discontinue the reactant ammonia-air flow whenever the temperature reaches 1000° C. and will instead admit immediately a rapid flow of cold air in order to cool the plant as fast as possible before any damage could occur.

Thermal Measurements of Sample Streams

Frequently, it may be advantageous to carry out the measurement of heat effects in sample streams instead of measuring them directly in the process stream. Generally thermal measurements can be carried out by combining the measurement of the temperature difference created by the reaction in the sample stream with that of the flow rate of the sample stream resulting in the "BTU rate" of the process. Commercial instrumentation for BTU-rate meters or for integrated BTU-values is available.[2] Although little use appears to have been made of this type of monitoring and control, it might be of interest, especially in processes involving streams of viscous materials, emulsions, or slurries, such as those occurring in polymerization processes.[2]

As another method of applying thermal measurements, the monitoring of the strength of nitration acid may be mentioned (as illustrated in FIGURE 2, left).[3] The nitration acid, which is a mixture of nitric acid and sulfuric acid, is passed intermittently through a sample line by means of a rotating valve into the measuring cell. During the periods which no nitration acid is flowing, measured and equal amounts of benzene are added to the acid. The heat of nitration of the benzene is measured by means of a platinum resistance thermometer wound directly on the outer wall of the reaction cell. The measurement of the resistance thermometer is carried out in a conventional way by a bridge circuit as shown in FIGURE 2 (right).

It is also possible to analyze a component in a sample stream by measurement of the heat with a specific reactant of a chemical reaction of the component to be analyzed. In many cases the reactant has to be added to the sample stream. Such reactions are frequently carried out catalytically by passing the sample stream over a suitable catalyst.

FIGURE 3 shows a device to determine and to monitor the content of oxygen in gas streams by catalytic reaction with hydrogen over a palladium catalyst.[4] Unless the gas stream to be analyzed already contains hydrogen, hydrogen is added to the sample stream from an electrolytic cell. The temperature difference of the gas before and after the catalyst is measured with a thermopile whose output can be fed into an electronic recorder-controller. The sensitivity of such a device is 2 ppm.

FIGURE 4 illustrates an application of this principle to monitor and to control the residual oxygen content in inert or reducing atmosphere, such as that used in steel mills. Oxygen-containing process gas is passed after addition of hydrogen through a catalytic purification unit and through driers. A sample of the treated process gas is continuously passed into the calorimetric-catalytic analyzer (E). The output of the calorimeter is fed to an electronic recorder-controller that in turn actuates a control valve to regulate the hydrogen supply required for the catalytic purification of the process gas. In this way the oxygen content of the purified gas is continuously monitored and maintained at a predetermined level.

Thermal Conductivity Measurements

A particularly versatile analytical method is based on thermal conductivity measurements of gases. The principle of a thermal conductivity cell is shown in FIGURE 5 and the basic circuitry in FIGURE 6. The essential component is an electrically heated filament or thermistor element exposed to the test gas slowly passing through the chamber. At equilibrium the heat losses due to radiation and the convection and conduction of heat equal the input of electrical energy. The sample chambers are normally designed for minimum radiation and convection losses. Thus the equilibrium temperature established, defining the resistance value of the filament, is essentially determined by the thermal conductivity of the surrounding gas. TABLE 2 contains values of the thermal conductivities of a number of gases and vapors of interest for analytical purposes referred to the thermal conductivity of air that at a temperature of 0° C. has a value of 0.000058 Cal./cm./° C.

Analysis is usually carried out either by comparing the temperature of the element in the unknown gas with that in a reference gas, usually air, or by passing the sample gas first through one measuring cell and, after scrubbing the

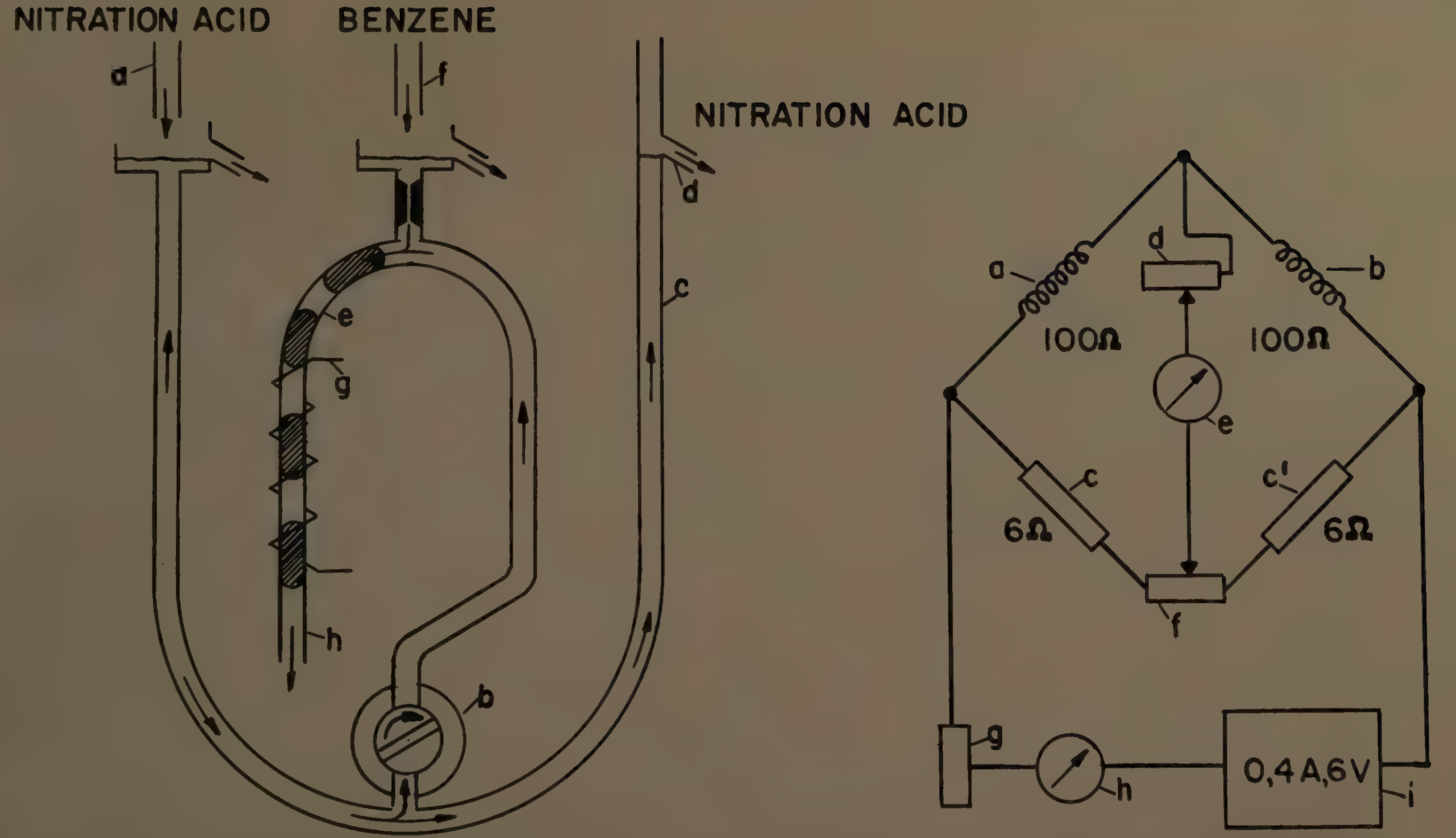

FIGURE 2. Instrument for monitoring strength of nitration acid by measuring reaction heat. (*Left*) *a*, nitration acid inlet; *b*, rotating valve; *c* and *d*, nitration acid effluent; *e*, reaction zone; *f*, benzene inlet; *g*, resistance thermometer; and *h*, nitrobenzene effluent. (*Right*) *a*, platinum resistance thermometer; *b*, comparison thermometer; *c* and c^1, resistors; *d*, sensitivity adjustment; *e*, indicator; *f*, zero adjustment; *g*, current adjustment; *h*, milliammeter; and *i*, constant voltage transformer. Reproduced by permission of the *Chemie-Ingenieur-Technik*.[12]

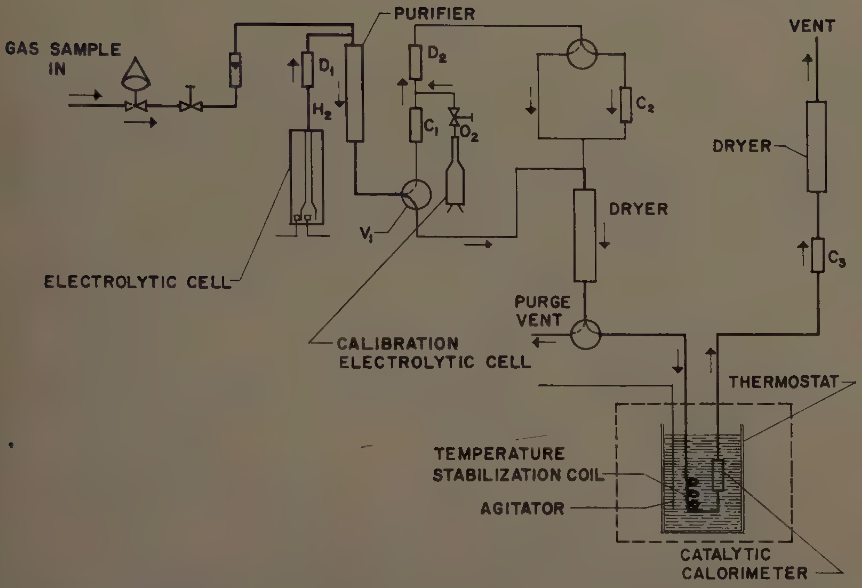

FIGURE 3. Instrument for continuous analysis of gaseous constituent by measuring heat of catalytic reaction.

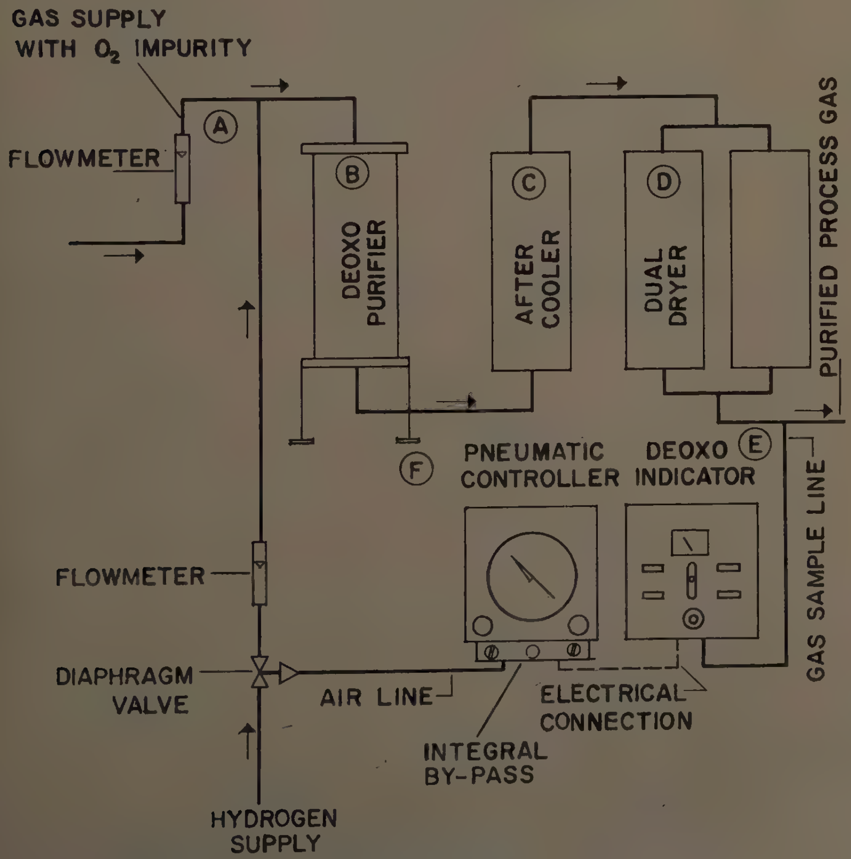

FIGURE 4. Monitoring and control of oxygen content of process gas by means of catalytic reaction instrument.

constituent to be analyzed, through a second reference cell (as indicated in FIGURE 6). Since the filaments or thermistors are connected in a Wheatstone bridge, any difference in the rate of heat loss from the elements in the two cells will cause the bridge to become unbalanced to an extent depending on the composition of the gaseous mixture. In general, thermal conductivity measurements are applicable only to binary mixtures or to gases in which the ratio of the components other than the component to be analyzed is constant. In order to use thermal conductivity measurements for multi-component mixtures,

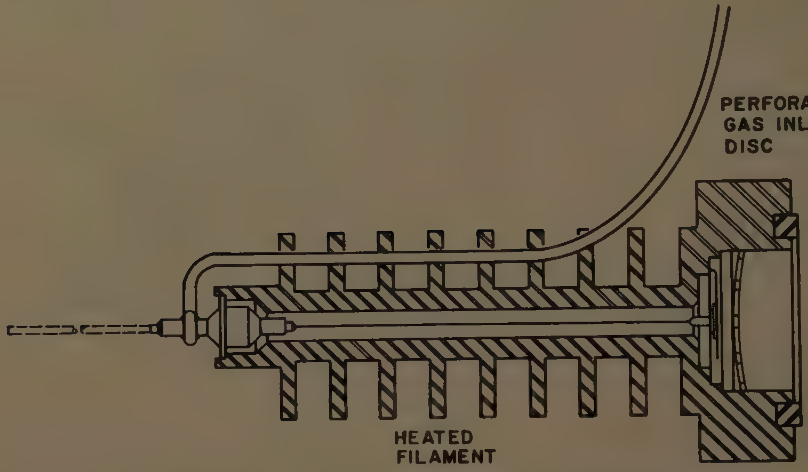

FIGURE 5. Basic structure of thermal conductivity cell.

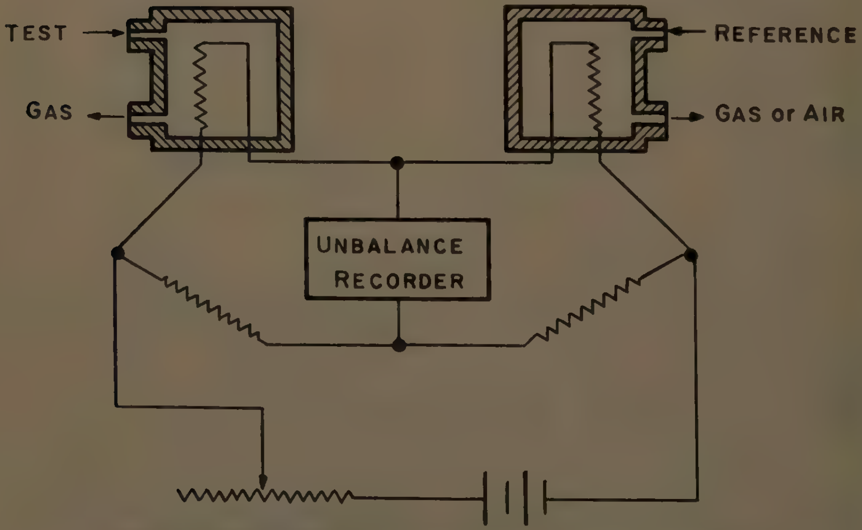

FIGURE 6. Bridge circuit for measurements of thermal conductivity.

TABLE 2

THERMAL CONDUCTIVITY OF GASES AND VAPORS

Gas	Temperature (° C.)	K gas/K air
Acetone	0	0.406
	100	0.557
Acetylene	0	0.777
	100	0.900
Air	0	1.00
	100	1.00
Ammonia	0	0.897
	100	1.04
N-Amylamine	0	0.479*
Argon	0	0.684
	100	0.696
Benzene	0	0.370
	100	0.583
N-Butane	0	0.552
	100	0.744
Butylamine	6.5	0.530
Butyl ether	100	0.534
Carbon dioxide	0	0.605
	100	0.700
Carbon disulfide	0	0.285
Carbon monoxide	0	0.960
	100	0.962
Carbon tetrachloride	100	0.288
Chlorine	0	0.323
Chloroform	0	0.269
	100	0.328
Cyclohexane	100	0.576*
Deuterium	0	5.85
Deutero ethane	0	0.635
Deutero methane	0	1.22
Deutero propane	0	0.523
Diethylamine	0	0.520*
Dimethylamine	0	0.610*
Di-N-propylamine	0	0.440*
Ethane	0	0.750
	100	0.970
Ethyl acetate	100	0.543
Ethylamine	0	0.583*
Ethyl alcohol	100	0.700
Ethyl bromide	0	0.295*
Ethyl chloride	0	0.391
	100	0.540
Ethyl ether	0	0.747
Ethyl iodide	0	0.242*
Ethyl butyl ether	100	0.625
Ethyl propyl ether	100	0.670
Ethylene	0	0.720
	100	0.980
Freon 12	0	0.344
Helium	0	5.97
	100	5.53
N-Heptane	0	0.582
N-Hexane	0	0.508
	100	0.662
N-Hexylene	0	0.431
	100	0.618
Hydrogen	0	7.15
	100	7.10

TABLE 2—*Continued*

Gas	Temperature (° C.)	K gas/K air
Hydrogen chloride	0	0.635†
Hydrogen sulfide	0	0.538
Isobutane	0	0.569
	100	0.776
Isobutylamine	0	0.511*
Isopentane	0	0.515
Isopropyl ether	100	0.642
Krypton	0	0.363
Methane	0	1.25
	100	1.45
Methyl acetate	0	0.421
Methyl alcohol	0	0.592
	100	0.727
Methyl bromide	0	0.257
	100	0.350
Methyl chloride	0	0.377
	100	0.530
Methyl iodide	0	0.194
	100	0.254
Methyl butyl ether	100	0.664
Methyl ethyl ether	100	0.772
Methyl propyl ether	100	0.716
Methylamine	0	0.657*
Methylene chloride	0	0.275
	100	0.329
Neon	0	1.90
	100	1.84
Nitric oxide	0	0.980
Nitrogen	0	0.996
	100	0.996
Nitrogen atmospheric	0	0.993
	100	0.993
Nitrogen dioxide	55	1.57
Nitrous oxide	0	0.646
	100	0.730
Oxygen	0	1.013
	100	1.014
N-Pentane	0	0.535
	100	0.702
Propane	0	0.615
	100	0.832
Propylamine	0	0.517*
Propyl ether	100	0.616
Propyl butyl ether	100	0.566
Sulphur dioxide	0	0.350
Triethylamine	0	0.457*
Trimethylamine	0	0.565*
Water vapor	100	0.775
Xenon	0	0.213

* Results reduced from a slightly different temperature by means of reported temperature coefficients or coefficients deduced from a homologous series.

† Computed values.

chemical scrubbing of interfering substances or of the component to be analyzed can be used as described above. In ternary or more component-containing systems it is also possible to employ conditions in which both thermal conductivity and convection effects are utilized to obtain response to a particular

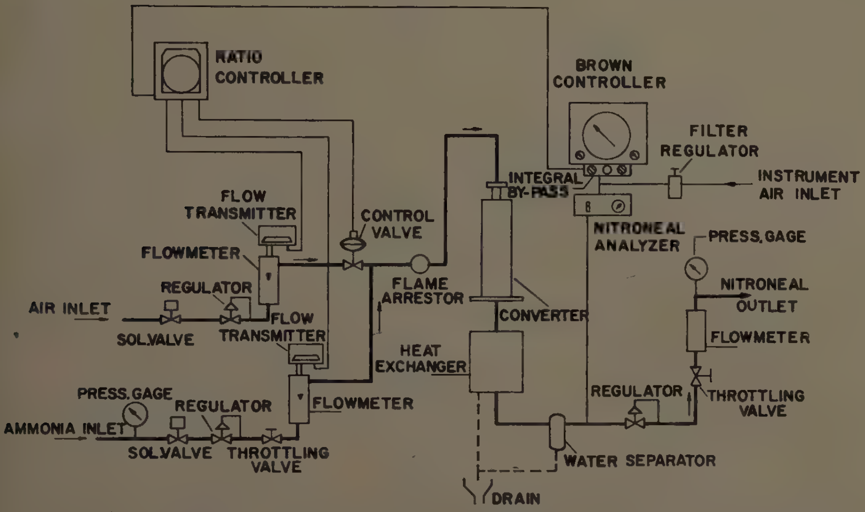

Figure 7. Monitoring and control of hydrogen content in nitrogen produced by catalytic combustion of ammonia employing thermal-conductivity instrument.

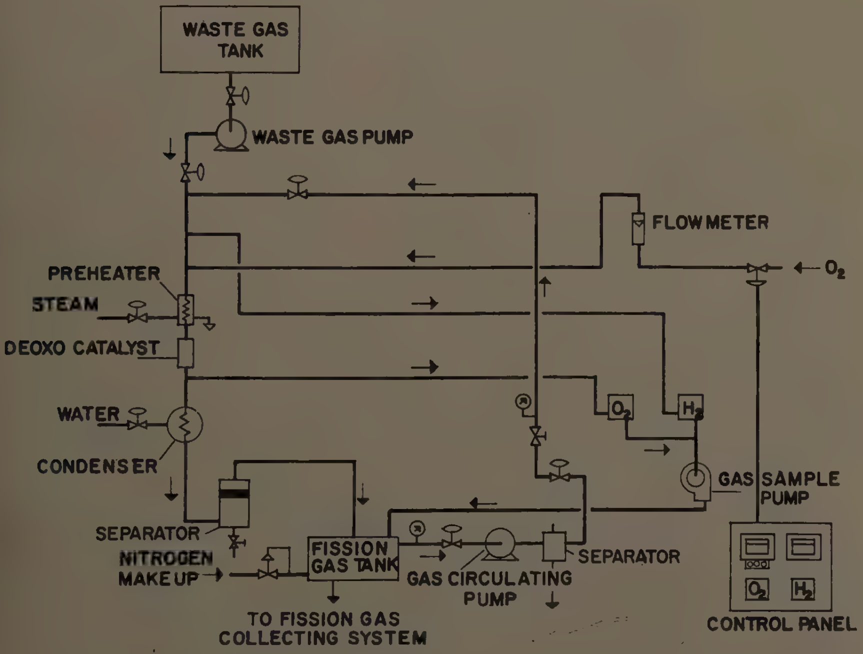

Figure 8. Removal of hydrogen from waste gases.

component. A practical instrument based on this principle has been described by Strange.[5] Depending on the nature of the sample, the threshold of detection may be as low as 100 or a few hundred volumes ppm. Measurements can be made with rapid response times.

Thermal-conductivity measurements can be used in many ways on chemical process streams. An example for an application is shown in FIGURE 7 referring to a generator for nitrogen or hydrogen-nitrogen mixtures by catalytic combustion of ammonia according to the reaction $2NH_3 + 1.5O_2 \rightarrow N_2 + 3H_2O +$ 92.5 kcal./M at 25° C.* The hydrogen component of the mixture is obtained by adding excess ammonia to the reaction mixture. The excess ammonia is cracked into hydrogen and nitrogen by the heat liberated in the oxidation reaction. The hydrogen content of the gas leaving the catalytic converter is monitored by a thermal conductivity instrument that in turn actuates a controller to adjust the air-ammonia ratio for a desired hydrogen content.

Another example of the applicability of thermal-conductivity analysis is the reduction of the hydrogen content in the waste gases of a nuclear power plant. Hydrogen has to be removed to allow concentration of the permanent radioactive fission gases for final disposal. The process is shown in FIGURE 8. The waste gas stream from the plant is diluted with nitrogen and, after addition of appropriate amounts of oxygen, preheated and passed over catalytic converters that combine the hydrogen with the oxygen. The water formed is condensed and the nitrogen recirculated. Thermal-conductivity measurements are used to monitor and to control both the oxygen content as well as the hydrogen content of the gas stream before and after the catalytic converter. All process equipment and the conductivity cells are located in the radioactive area, whereas the monitoring recorders are located outside this area and accessible to the plant personnel.

Thermal-conductivity measurements are also useful for cases where the process stream itself may not involve gases. For instance, a continuous recording of the concentration of organic matter in waste water streams has been described by Kieselbach.[6] In this application, the waste water is pretreated to remove the carbon dioxide, subsequently the organic matter is oxidized with a mixture of chromic and sulfuric acid to form carbon dioxide, which is carried by means of an oxygen stream through a thermal-conductivity cell and measured differentially by passing the scrubbed oxygen CO_2 free through the reference cell. With this method, carbon concentrations of 1 ppm. can be detected in the water and can be continuously monitored.

Thermal Properties of Potential Usefulness

There are a number of thermal measurements that potentially could be applied or developed for continuous automatic monitoring. Several of such applications may be mentioned.

Measurement of temperature of complete miscibility of liquids. Mosley, *et al.*[7] have described a method of determining the temperature of complete miscibility of two liquids on an automatic, continuous basis. By subjecting the sample to automatic heating and cooling cycles, the point of miscibility can be found by photoelectric measurement of the turbidity that obtains in the state of immiscibility. Since the temperature of miscibility may vary with the concentration of a specific component, it appears feasible to achieve continuous analysis by adding to a liquid sample stream another liquid and obtaining the concentration of the component in question by passing the combination through a turbidity recorder.

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* Rosenblatt, E. F. & G. Cohn. U. S. 2,606,875.

Thermal titration. Thermal titrations measuring the heat developed upon adding the titrant have been described repeatedly. In common with conductometric titrations, the end point of thermal titrations is usually poorly defined. A method developed by Zenchelsky and Segatto[8] avoids this shortcoming by recording the derivative function of the temperature developed during titration. Such analysis may be adaptable for practically continuous determination of an acid or a base in a sample stream.

Thermogravimetric analysis. Solid materials undergoing at certain temperatures decomposition reactions with liberation of gases or reacting with gases may be characterized by the specific change in weight accompanying the reaction. Various recording thermogravimetric balances have been described, among them a torsion balance operable in vacuum or at gas pressures up to 600 psi with a response time of 2 sec.[9] Owing to the weighing speed obtainable, thermogravimetric analysis might in certain cases be adopted for monitoring on a nearly continuous basis the quality of a solid reaction product produced.

Differential thermal analysis. Solids may also be defined by differential thermal analysis. Any physical or chemical transformation involving a change of thermal energy can be identified by means of heating curves in which the temperature of the sample is continuously compared with that of a thermally inert reference material. Sample and reference material being heated in the same furnace the temperature differentials between them due to differences in heat capacity, heat conduction can be registered or monitored with thermocouples or thermistors. At a temperature at which a physical or chemical change of the sample occurs, the corresponding effect due to heat absorbed or generated during this transformation causes discontinuity—maximum or minimum—of the temperature-differential curve. Differential thermal analysis has been widely used in the study of solids, in particular with respect to detection of such transformations and their kinetics. A survey of the field has been given by Smothers and Chiang.[10] Among recent contributions to experimental techniques the description of a thermistorized apparatus[11] may be mentioned and a discussion by Campbell *et al.*,[12] who developed instrumentation for recording of derivative functions, the latter being especially useful in thermogravimetry. Conceivably, differential thermal-analysis equipment could be designed with sufficient response speed to make possible its application for almost continuous monitoring of solid products in a process stream.

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Part III.

INTRODUCTORY REMARKS

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In recent years there have been many advances and increased use of volumetric and/or colorimetric analysis, atomic radiation and absorption measurements, and the continuous analyses of oxygen.

The use of radiant energy in the visible range has been increasing in popularity in the design of chemical analyzers. Sixty-four years ago, Henri Becquerel discovered radioactivity and, since World War II, great strides have been made in the use of this technique for analytical purposes. The continuous analyses of oxygen is of major importance to many of our industries. There are many approaches by which these analyses may be performed. The selection of the proper one is dependent upon many factors.

The contributors to this section present their papers with the philosophy and the principles for both proper design and the selection of a given system for a given problem in mind. It is hoped that you will profit from their dissertations.

AUTOMATIC CONTINUOUS MEASUREMENT OF OXYGEN

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Continuous monitoring of cryogenic process streams is a relatively new field of analysis. The main products of cryogenic processes are argon, oxygen, nitrogen, helium, and, more recently, liquid hydrogen. In the manufacture of most of these products, the continuous measurement of low concentrations of oxygen is required. In oxygen production, oxygen is obviously the major component.

Sample-Point Selection

Although the products of cryogenic processes are usually in gaseous form, many monitoring points within the process are at cryogenic liquid temperatures. This fact requires that sample point selection be given careful consideration since most continuous monitoring analyzers require a gaseous sample.

Because of the problems involved in converting a cryogenic liquid from a process stream to a representative vapor sample, gaseous samples that represent liquid streams are selected where possible. Where this is not possible, apparatus must be utilized for converting a liquid completely to a vapor without changing its composition. Consideration must also be given to sample-point selection depending upon the purpose of the analysis. Analysis may be required for determining the purity of the product, determining the impurities in the product, or determining the performance of equipment in the process.

An example of sample-point selection may be discussed in connection with the production of liquid hydrogen in which efforts are made to make certain that no oxygen or oxidizing agents enter the process. At one of the liquid hydrogen production facilities we operate, the feed is the off-gas from a chlorine production facility. The hydrogen from this facility contains a number of impurities including small quantities of oxygen. These traces of oxygen are removed by conversion to water over a catalyst bed. As may be seen in FIGURE 1, the crude hydrogen gas enters the plant, passes through a charcoal adsorber to remove acid gases and other impurities, and then passes through a deoxo-catalyst bed. The oxygen, in the presence of the hydrogen, is converted to water. The water is removed in a trap and the hydrogen gas is fed to the compressor. To guard against the possibility that additional oxygen might enter the stream during the compression stages, a second, high-pressure deoxo-catalyst bed, is placed in the stream immediately after the compressor and its driers. Sample-point selection is made as indicated in FIGURE 1, and gas from these two sample points is fed alternately—by the use of a cam timer and solenoid valves—through a trace oxygen analyzer to determine the performance of the catalyst beds. A small tube connected through a solenoid valve that bypasses the first (low pressure) deoxo may be noted in the figure. This bypass was installed after the plant had been in operation for some time. During the initial operation of the plant the trace oxygen analyzer, which had a range of 0 to 25 ppm oxygen, indicated a zero oxygen content regardless of the sample being fed to the analyzer. The only time the analyzer moved from the zero point was during the "span operation" that was carried out automatically once each hour. The operators of the plant lost confidence in the instrument since it always indicated a zero concentration. In order to assure ourselves and the operators that the instrument was performing properly, during each cycle of sample analysis the solenoid valve in the bypass was activated, and a portion of the hydrogen containing oxygen was allowed to bypass the No. 1 deoxo. This oxygen, which gave an indication on the analyzer chart of 3 to 4 ppm was then removed by the high-pressure deoxo. As may be seen from the representative strip chart depicted in FIGURE 2, there is no indication of oxygen while monitor-

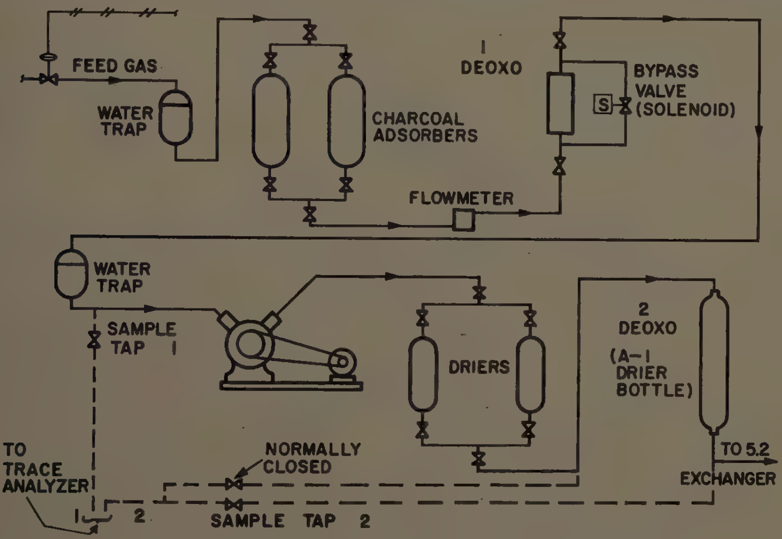

FIGURE 1. Trace oxygen analysis in typical liquid hydrogen plant.

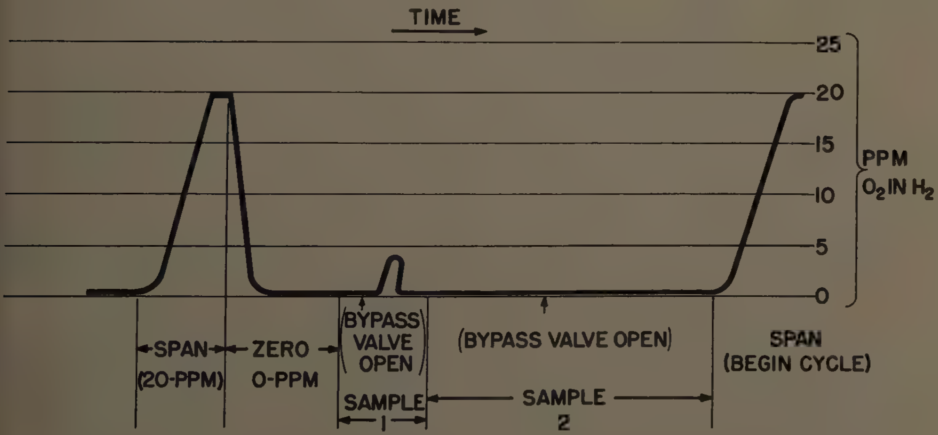

FIGURE 2. Representative strip chart trace oxygen analyzer.

ing Sample 2. This type of intermittent-impurity injection gave the operators and the engineers confidence in the analyzer.

A second example of proper sample-point selection may be taken from a liquid oxygen and liquid nitrogen production facility as utilized by the United States Air Force for its missile program. In this case the majority of the analytical requirements for the operation of the plant is accomplished with three multisample continuous monitoring analyzers. These are a paramagnetic analyzer for the determination of small quantities of oxygen in nitrogen, a thermal conductivity analzyer for the determination of the oxygen purity in the oxygen product, and a total hydrocarbon analyzer for the determination of the carbon dioxide and hydrocarbon content in various portions of the process stream and in the oxygen product.

Liquid oxygen and liquid nitrogen plants utilize many methods to remove impurities. The incoming air is compressed. Intercoolers, separators or knockout pots, and desiccant beds are employed to remove moisture and oil. Some soluble and occasionally some insoluble hydrocarbons are carried into the rest of the plant with the incoming air. As the air is cooled in exchangers, expanded, and liquified, these hydrocarbons and other contaminants such as carbon dioxide are carried along with the liquid. In the particular plant being considered, the carbon dioxide, which has a very low solubility at liquid air temperatures (approximately 5 ppm), is removed in a porous filter. The hydrocarbons are adsorbed at liquid air temperatures in silica gel adsorption beds. The purified liquid air is then further expanded to a lower temperature and separated in a distillation column. Liquid oxygen is removed from the bottom of this column and waste nitrogen, some of which is used for reactivation, is removed from the top of the column. High-purity nitrogen is removed from near the top of the high pressure column that is in the process stream prior to the filtering and adsorbing equipment previously mentioned. When nitrogen product is not being made, the higher purity nitrogen is utilized entirely for reflux in the high- and low-pressure columns. The three analyzers are used to monitor the plant (see FIGURE 3) as follows:

The hydrocarbon analyzer monitors three different samples in a timed sequence. The first sample point is in the high-pressure air following the drier and prior to any cooling. This sample gives information concerning the possibility of excessive lubrication or of unusual hydrocarbon contamination entering the plant from the atmosphere. The second sample point requires an accessory sampling apparatus to convert the rich-air liquid to a representative vapor sample. The need for the separator-vaporizer will be discussed later. This analysis point is located in the process stream just after the carbon dioxide filters and hydrocarbon adsorbers and gives an indication of the performance of these units and the need for their reactivation or regeneration. The third point procures a sample from the liquid product oxygen and also utilizes the separator-vaporizer accessory to give an indication of the product's carbon dioxide and hydrocarbon content.

The nitrogen analyzer may analyze one or more samples, but selection is manual depending on the plant operation. When the plant is producing oxygen, a vapor sample taken above a tray near the top of the high-pressure column is utilized. The range of the instrument is set at 90 to 100 per cent, and the analysis is utilized for purity control purposes. The nitrogen represented by this vapor sample is liquified in the trays of the column and supplies reflux to both the high- and low-pressure columns. The second sample that can be fed to this analyzer is a vapor sample representative of the top of the low-pressure column. The cold vapor (the waste nitrogen) is exchanged against the incoming air to cool the incoming air and may be procured as a warm gas for analysis. This waste nitrogen is used as a reactivation gas for the adsorbers and dryers or is vented to atmosphere. In reactivating hydrocarbon adsorbers, a low oxygen content is required for safety reasons; hence the need for monitoring this gas. When the plant is producing nitrogen, it is operated to obtain liquid of 99.5 per cent purity from the top of the high pressure column. The second range of the analyzer (98 to 100 per cent) is utilized during this analysis to determine if the plant is producing a 99.5 per cent purity liquid.

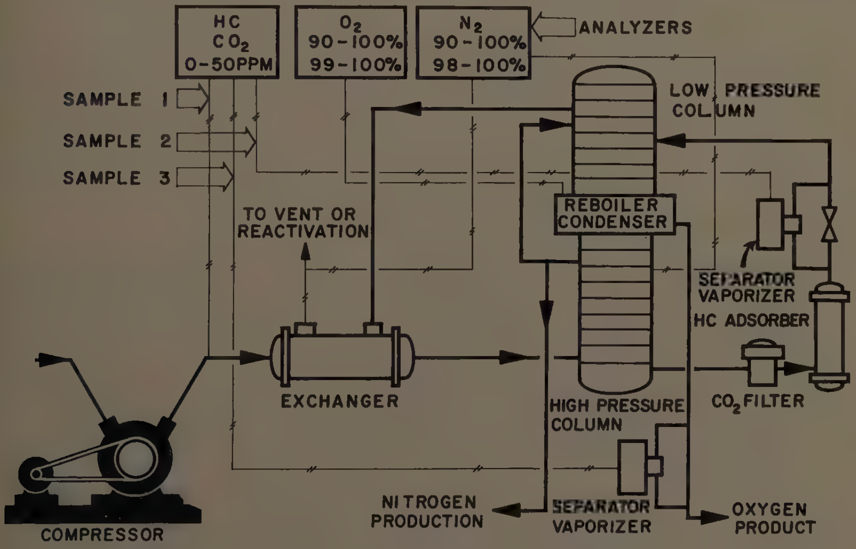

FIGURE 3. Typical liquid oxygen plant sample point selection.

The third analyzer, the oxygen purity analyzer, procures its sample from the vapor space in the condenser-reboiler and is utilized to monitor the oxygen product purity. The liquid oxygen product is the liquid in the condenser-reboiler. This analyzer is also dual range 90 to 100 per cent and 99 to 100 per cent. The 90 to 100 per cent range is used when the plant is brought "on-stream," and the 99 to 100 per cent range is used during production.

From these two examples, it may be seen that the main rules to follow in proper sample point selection in cryogenic processes are:

(1) Sample points are always necessary to monitor product purity.

(2) Sample points are usually necessary to monitor contaminant-removal equipment and process equipment.

(3) Wherever possible, if a cryogenic liquid or cold vapor is to be monitored, determine if the sample might be procured as a "warm" vapor in some other

portion of the plant. The gaseous sample procured in this manner should accurately represent the liquid or cold vapor.

(4) Monitoring of products or process equipment where build-up of dangerous contaminants could occur is always necessary for personnel safety reasons.

Sampling

There are many problems involved in the conversion of a cryogenic liquid to a representative vapor for analysis. Almost all of the analytical techniques for monitoring cryogenic process streams require vapor samples. Since in some instances the only stream that can be utilized for monitoring is a liquid, techniques for converting a cryogenic liquid to a vapor, without changing the concentration of the liquid including any contaminants that might be present, have been developed.

The physical factors that must be considered in obtaining vaporization without change in concentration are: the solubility of contaminants present; the vapor pressure relationships between the liquid and the contaminants, either solid or liquid; and the possibility of fractional distillation occurring during vaporization. In order to explain these factors, analysis for the carbon dioxide present in the liquid air downstream of the filtering and adsorbing equipment as shown in FIGURE 3 will be considered as a typical example. If the carbon dioxide content of the liquid exceeds its solubility limit of approximately 5 ppm, solid carbon dioxide will be present in the stream. If a liquid sample withdrawn from this stream is allowed to vaporize in the sample "tap" line to produce a vapor sample for the analyzer, the initial vapor at the analyzer would be carbon dioxide lean. Very little of the carbon dioxide would vaporize because of its lower vapor pressure at liquid air temperature. Successive vaporization and condensation of this liquid sample may also occur as it traverses the sample tap line and, occasionally, large slugs of carbon dioxide vapor might pass through the sample vapor line resulting in an extremely erratic analysis record. Soluble hydrocarbons (such as methane), which are present in the stream, may change in concentration due to fractional distillation as the liquid traverses the vaporization coil (sample tap) so that vapor reaching the analyzer could also be lean in its hydrocarbon content. In addition, the process stream in this portion of the plant is a mixture of vapor and liquid. If a simple sample tap were utilized to sample this stream, during a portion of the analysis, some vapor would enter the sample vaporization line and this vapor would also be lean in the higher-boiling contaminants, such as methane, carbon dioxide, and nitrous oxide.

An apparatus was therefore required for separating the vapor from the liquid and then vaporizing all (or a portion) of the liquid before fractionation or other changes could occur. In FIGURE 4 may be seen a schematic diagram of the separator-vaporizer that has been developed. The mixed sample of liquid and vapor enters the apparatus at A and proceeds to the inner chamber of the separator. As may be seen in Section A-A, which is a cross-section of the separator portion of the apparatus, the liquid enters the inner container tangentially with a swirling effect. This effect helps to keep any solids well dispersed through the liquid. Vapor, plus liquid, exits through the overflow tube in the center of the inner chamber, and the liquid fills the outer chamber.

The inner-chamber liquid, being surrounded by liquid at approximately its same temperature, is prevented from vaporizing. Gas, plus liquid, leaves through the outlet of the separator portion of the apparatus and this flow is controlled by the metering valve. The excess vapor and liquid is routed to a lower pressure portion of the plant. In the case of monitoring the carbon dioxide filtering and hydrocarbon adsorbing equipment, this apparatus is conveniently mounted "around" the "O-1" valve with an 80-psig inlet pressure (high-pressure column pressure) and an 8-psig (low-pressure column) outlet pressure. The liquid separated passes into the lower vaporizer portion of the apparatus and drips onto the heated high surface area plate. A number of small brass hexagonal head nuts are placed in the lower chamber where they may be in contact with the heater plate and supply the warming surface area required. The vaporized sample then flows out through the vapor sample outlet to the analyzer. Control of the portion of liquid vaporized is performed by controlling the flow of vapor to the analyzer. The development of this apparatus, which has been termed the Separator-Vaporizer, required a tremendous amount of experimentation and on-site plant analysis. It is the only apparatus we know in which we have confidence for accurately converting a cryogenic liquid mixture to a representative vapor sample. These apparati are utilized wherever it is necessary to monitor continuously a cryogenic liquid stream with higher-boiling contaminants by gas analysis.

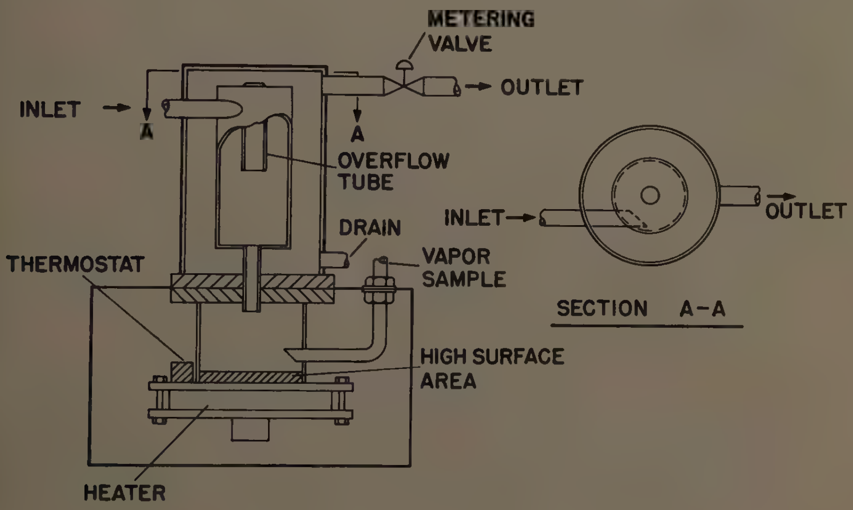

FIGURE 4. Separator-vaporizer sampler.

Analytical Methods

Various continuous monitoring techniques are available for the determination of oxygen and the contaminants in oxygen in cryogenic process streams. The choice of the proper technique is dependent on the level of oxygen present in the stream or the type contaminant to be measured.

Normally a thermal conductivity or paramagnetic technique is used in the measurement of oxygen purity. The paramagnetic technique is also used to measure a low percentage of oxygen in a nitrogen stream. Trace oxygen analyzers utilize the Hersch Cell principle or a catalytic heat of formation of water technique for the determination of trace quantities of oxygen in a hydrogen, nitrogen, or argon product. We have developed our own analyzer for the determination of hydrocarbons and carbon dioxide, which are the major trace contaminants in an oxygen product stream.

Paramagnetic analyzers. Oxygen is unique among other gases in that it is highly paramagnetic and, as a result, will increase the magnetic flux density when it is present in a given magnetic field. This principle is the basic concept of the paramagnetic analyzer.

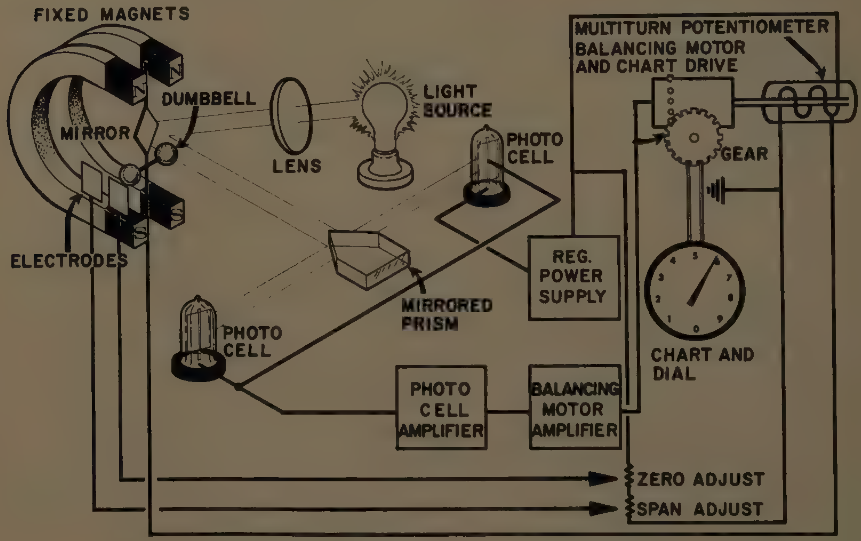

FIGURE 5. Paramagnetic analyzer schematic.

The analyzer test unit in a typical paramagnetic analyzer (FIGURE 5) is constructed as follows. A lightweight dumbbell is supported on a quartz fiber between magnetic pole pieces. Each sphere of the dumbbell is in a nonuniform magnetic field. The dumbbell assembly itself has a fixed magnetic susceptibility that is held at a null point by fixed magnets and two metal electrodes or vanes near the test body. These electrodes are maintained at fixed electrical potentials, producing in effect, a heterostatic electrometer. When a sample gas-containing oxygen surrounds the dumbbell suspension, the suspension experiences a force dependent on the difference between the magnetic properties of the test gas and the suspension itself. The effect of the force tends to rotate the dumbbell about the quartz fiber on which it is suspended and the magnitude of this force is proportional to the oxygen content of the sample gas. As can be seen in the figure a light-dividing mirror divides a light beam to the photo tubes in equal proportions when the dumbbell and its mirror are in the null position. When the dumbbell rotates due to a change in the oxygen content of the gas surrounding it, the light to the photo cells is divided unequally and this produces a voltage change. The voltage change drives a balancing motor forward or backward depending upon the direction of rotation of the test body. The balancing motor in turn drives the recorder indicator and a variable potentiometer, causing a change in potential on the electrodes at the test body source (dumbbell). The dumbbell then returns to its original or null point, the potential required to return it being equal to the change in oxygen content. With the use of this type of null-balancing potentiometer system, changes in the rotation of the dumbbell due to changes in oxygen content can be indicated on a recorder as oxygen percentage. Instruments based on the utilization of this unique property of oxygen are the most commonly used in oxygen purity monitoring.

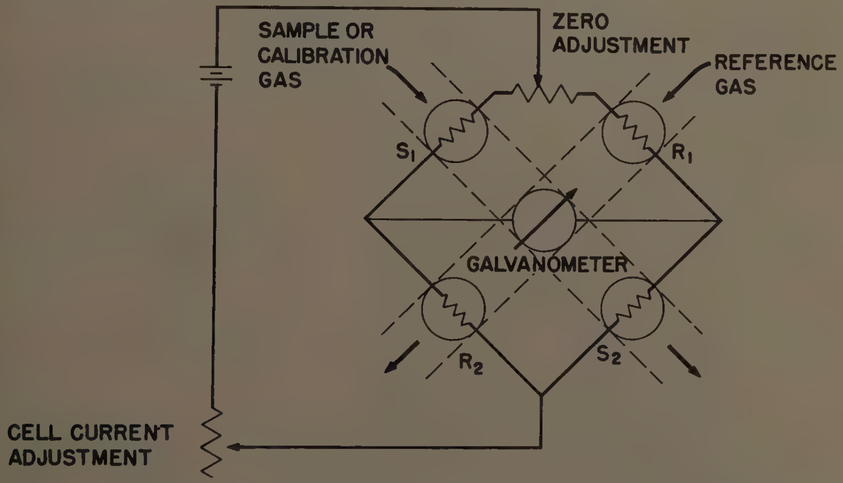

FIGURE 6. Typical thermal conductivity analyzer schematic.

Thermal conductivity. Oxygen purity analysis by thermal conductivity (FIGURE 6) is based on the fact that, if a wire surrounded by a gas in a closed chamber is connected to a constant source of voltage, the temperature of the wire will change until the continuous loss of heat (thermal energy) from the wire has reached a steady-state condition. Thermal energy is dissipated by radiation, thermal convection, and conductivity through the gas surrounding the wire. If a thermal conductivity cell is properly constructed, radiation and convection will account for only a minute portion of the loss of thermal energy. The equilibrium temperature attained by the wire, therefore, would be almost entirely a function of the thermal conductivity of the gas surrounding the wire. In thermal conductivity cells, filaments are used that have high temperature coefficients of electrical resistance. This resistance will vary at thermal equilibrium, according to the gas thermal conductivity, and therefore according to the composition of the gas surrounding the wire. Normally, the high-resistance wires are the resistors in a Wheatstone Bridge for gas analysis. In this type of configuration, a quantitative determination of an impurity present in a gas may be accomplished if the thermal conductivity of the impurity is considerably different from the thermal conductivity of the pure gas. For example, argon is the major impurity in product oxygen and, since its thermal conductivity is considerably different from that of oxygen, the analysis of oxygen purity by this technique is easily accomplished. If there is a chance that nitrogen might also be present with the argon in the oxygen, the total argon and nitrogen impurity cannot be determined since the thermal conductivity of nitrogen is very similar to that of oxygen.

Deoxo principle. As stated previously, trace oxygen analyzers are required to determine the oxygen contamination in nitrogen, argon, or hydrogen. This analysis is normally accomplished by one of two means: through the use of an analyzer that encompasses the Hersch Cell principle or one that determines the oxygen by the catalytic heat of conversion of the oxygen to water or the "deoxo" principle. In a typical deoxo analyzer (FIGURE 7) the sample containing the oxygen enters the analyzer, passes through a purifying tower and then a drying tower. An excess of hydrogen is added to the sample (this hydrogen is formed by electrolysis in an electrolytic cell). The sample then passes through a constant temperature bath and into a bed containing a catalyst. The oxygen and hydrogen that has been introduced in the presence of the catalyst is converted into water. This reaction is exothermic, and the heat generated is measured by a thermopile inserted in the catalyst chamber in the calorimeter. The amount of heat generated is directly proportional to the amount of oxygen originally present in the sample. The other flow and valve system depicted in the figure is utilized in zeroing and calibrating the analyzer. Zeroing is accomplished by removing all the oxygen present in the stream by passing it through a catalyst chamber prior to the sample's entry into the calorimeter. With no oxygen present, the analyzer can be adjusted to give a zero indication. The analyzer is calibrated by introducing a known

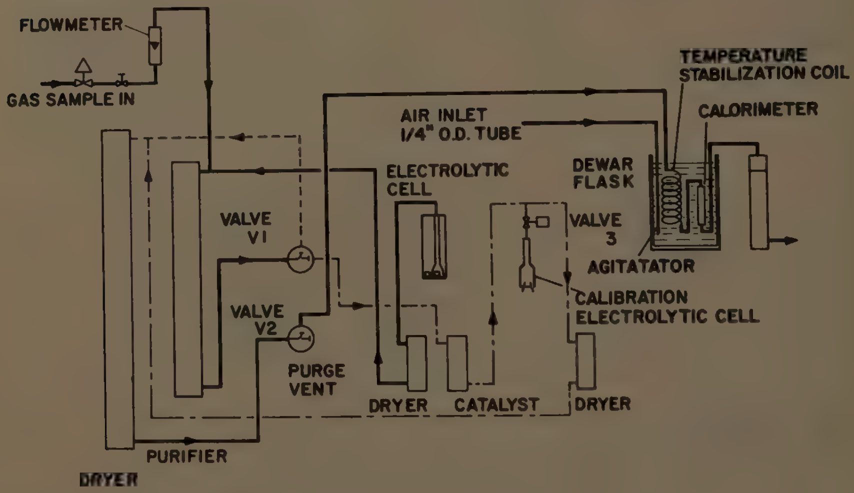

FIGURE 7. Typical deoxo analyzer schematic.

quantity of oxygen into the zero gas stream through the use of a calibration electrolytic cell, wherein a known current on the electrodes of the cell provides a known volume of oxygen according to Faraday's Law. This type of analyzer may be sensitized for multiple-range analysis varying from 0 to 200 to 0 to 2000 ppm oxygen full-scale. Where minute quantities of oxygen must be determined, this technique will not suffice since the minimum detectable limit is only 2 ppm. By reversing the polarity on the electrolytic cell, the analyzer may be used to detect trace quantities of hydrogen in process streams. The cryogenic industries' main use of this analyzer has been in the detection of trace quantities of oxygen in nitrogen and argon product streams.

Hersch principle. Rather than describe any particular analyzer, the Hersch Cell principle of galvanic cell trace oxygen analysis will be described. FIGURE 8 depicts a schematic Hersch Cell analyzer concept. The analyzer embodies a galvanic cell with an inert cathode such as silver and a lead or cadmium anode. The electrolyte is a dilute caustic, usually potassium hydroxide. Oxygen present in the gas stream is chemisorbed on the surface of the silver electrode and is dissociated on the surface to nascent or monatomic oxygen. At the interface of the electrolyte, the silver cathode, and the gas, solution of the oxygen takes place, and it is ionized with a gain of two electrons to form two hydroxyl ions for each atom of oxygen reacted. The hydroxyl ions react at the anode and, if the anode is lead, form the plumbite ion plus water and two electrons. The electron flow is from the anode to the cathode; the current flow conversely is from the cathode to the anode. With proper standardization of known gases, the current flow can be calibrated to indicate oxygen quantity. Calibration may also be accomplished through the use of two electrodes in a caustic solution (a galvanic cell) that can introduce a known quantity of oxygen into the incoming sample by impressing a current on the

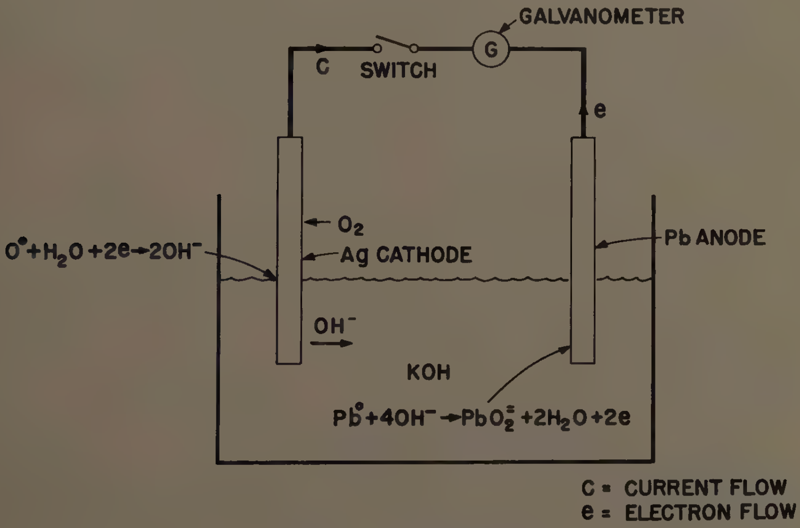
GALVANOMETER
G
C
SWITCH
e
O_2
Ag CATHODE
$O^{\circ}+H_2O+2e \rightarrow 2OH^-$
Pb ANODE
OH^-
KOH
$Pb^{\circ}+4OH^- \rightarrow PbO_2^{=}+2H_2O+2e$
C = CURRENT FLOW
e = ELECTRON FLOW

FIGURE 8. Typical Hersch Cell.

electrodes according to Faraday's Law. This caustic solution in the galvanic cell is also used to remove impurities that might poison the cathode in the Hersch Cell. Since the sample is bubbled through this solution and the standardization galvanic cell plus the Hersch Cell are held at the same temperature in a constant-temperature bath, the sample is preconditioned by humidification so that there is no chance of changing the caustic strength in the Hersch Cell due to vaporization of its water content. The Hersch Cell trace analyzer has been found to respond more rapidly and to have a higher sensitivity than the deoxo principle of trace oxygen analysis.

Total hydrocarbon and carbon dioxide analyzer. Early in 1957 our company felt the need for a continuous monitoring tool to determine the hydrocarbon content of oxygen process streams including liquid oxygen product and oxygen-rich air. The total hydrocarbon analyzer concept developed at that time was not developed solely for the monitoring of hydrocarbon in oxygen as a safety measure. With the advent of tonnage production and its economical split-cycle plant and carbon dioxide filtering equipment, the continuous monitoring of carbon dioxide in oxygen and liquid air process streams was also deemed necessary. This second analytical requirement lent itself well to our concept of total hydrocarbon analysis.

To acquire the sensitivity we felt necessary for this type of monitoring, our only choice at the time was through the utilization of a Luft-Principle infrared analyzer. Since the hydrocarbons in a cryogenic process stream are present as a mixture and not one particular hydrocarbon, it was almost impossible to sensitize a detector for this mixture because the ratio of the varying hydrocarbons present in the process stream would change from time to time. For example, if we sensitized our detector for a mixture of 90 per cent methane and 10 per cent ethane, the actual methane and ethane present in the process stream might be at a 50:50 ratio resulting in an inaccuracy of the analysis.

In Luft-Principle infrared analysis, carbon dioxide may be determined in the presence of hydrocarbons and moisture if proper filtering is utilized. If all of the hydrocarbons present in the stream could be converted to carbon dioxide, then the total hydrocarbon content could be analyzed with a carbon-dioxide sensitized infrared analyzer. By sequencing the converted sample with a sample that had not been converted, the carbon dioxide content of the sample could also be determined by difference. A catalyst furnace was developed that, in the presence of oxygen, converted all of the hydrocarbons present to carbon dioxide.

In FIGURE 9 may be seen a functional schematic diagram of our most recent model total hydrocarbon analyzer. The analyzer accepts one of three samples, passes the sample directly into the sample cell with zero gas flowing through the reference cell to determine the original carbon dioxide content in the sample. By proper switching of solenoid valves the sample can be passed through the catalyst furnace that converts all of the hydrocarbons present to carbon dioxide with a resultant increase in carbon dioxide content. This increase in carbon dioxide is equivalent to the number of carbon atoms present in the sample on a molar basis, hence the name Total Hydrocarbon Analyzer. Sample flow may also be arranged to determine the hydrocarbon content irrespective of the carbon dioxide present in the gas by passing the sample that has not been catalyzed through the comparison or reference cell and the sample that has been catalyzed through the sample cell. Facilities are also available in the analyzer to sequence zero gas automatically through both the comparison and sample cell to zero the analyzer. To calibrate the analyzer, zero gas is introduced into the comparison cell, and a carbon dioxide reference standard

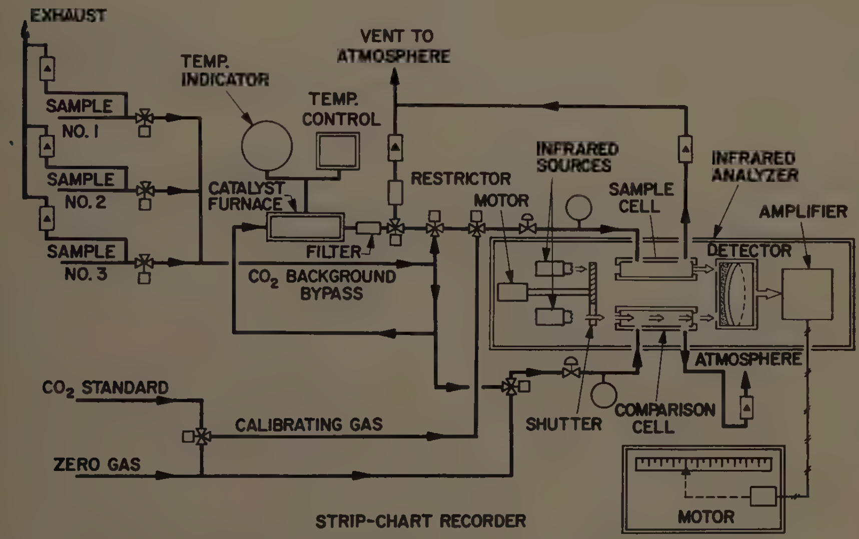

Figure 9. Continuous total hydrocarbon analyzer functional schematic diagram.

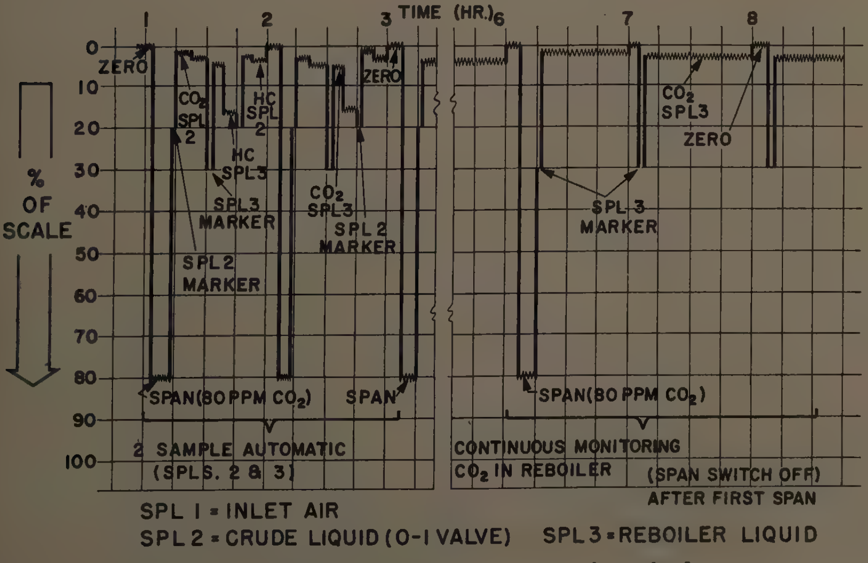

Figure 10. Hydrocarbon analyzer representative strip chart.

gas is introduced into the sample cell. This is a multiple-range analyzer with ranges varying from 0 to 30 to 0 to 400 ppm full-scale carbon dioxide.

Figure 10 is a representative strip chart from a 3-sample total hydrocarbon analyzer as used on a 25-T/D Air Force liquid-oxygen plant. The portion of the chart on the left shows the analyzer automatically switching between Sample 2 and Sample 3 with an automatic zero and span once each hour. The chart on the right shows the analyzer monitoring the carbon dioxide content in the reboiler, which is Sample 3 or the product oxygen continuously. From this it can be seen that facilities are available in the analyzer to change the sequencing or to eliminate portions of the analysis sequence as required.

Conclusions

Automatic continuous measurement of oxygen as related to cryogenic process manufacture can be adequately accomplished only with a combination of proper sampling methods and analytical techniques. Physical and chemical factors that affect the contaminant concentration or purity in the conversion of a cryogenic liquid process stream to a useable analysis vapor must be recognized. Where necessary, special equipment must be utilized to accomplish the liquid-to-vapor transition without changes in constituent molar content. As in any type of continuous process monitoring, the selection of analytical techniques and sample points is dependent on the level of contaminant or purity anticipated and the necessity of analysis as established in plant process design.

Part IV.

AUTOMATIC CONTINUOUS MEASUREMENT OF MOISTURE

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Water may exist as a gas, liquid, or solid. A number of instruments based on the physical state of water may be used for its measurement. The instrument used will depend upon the physical state of the water and other materials present in the system. The most widely used process instruments for moisture measurement use either optical, electrical, thermal, or nuclear detectors.

Optical moisture-measuring instruments include the dewpoint photoelectric analyzers and the refractometers, or near-infrared analyzers.

Dewpoint is defined as the saturation temperature or temperature at which liquefaction of a vapor begins. The dewpoint photoelectric analyzer is based on the measurement of the temperature at which condensation of moisture occurs. The dewpoint temperature is given in terms of the condensation temperature at a given temperature and pressure. A curve showing the relationship between dewpoint and actual concentration of moisture in parts per million by volume is shown in FIGURE 1.

Continuous process instruments used for measurement of dewpoint usually consist of a thermostated mirrored surface upon which the water vapor may condense and to which a temperature measuring element is attached (FIGURE 2). The mirrored surface may be cooled by expanding gases or mechanical refrigeration to the desired condensation temperature. Gases from the system are passed over the mirrored surface at a controlled rate of flow. The condensation temperature of moisture on the mirrored surface may be measured by a suitable photoelectric detector. Appropriate electronic circuitry, which indicates the dewpoint temperature will automatically control the temperature of the cooled mirrored surface so that one may obtain a reading of the dewpoint in terms of the indicated temperature.

Moisture may be measured in a liquid mixture when there is a difference in the refractive index of the water and other liquids present. The accuracy and limitations of this type of instrumentation is limited to the sensitivity of the apparatus, the solubility of the liquids in the mixture, and the change in refractive index over the given composition range.

The water concentration of process liquid streams that have been analyzed by process refractometers include such mixtures as: water in acetic acid, water in methyl alcohol, water in ethyl alcohol, water in ethylene glycol, water in sulfuric acid, and water in sugar.

Perhaps the most useful process type of refractometer is the differential refractometer that measures the change in refractive index between a liquid mixture and a reference liquid sample. This type of instrument permits highest sensitivity.

FIGURE 3 shows a schematic of the differential refractometer cell. A liquid sample is passed into the sample cell. The sample cell contains another cell that is filled with a reference liquid of a known refractive index. The sample

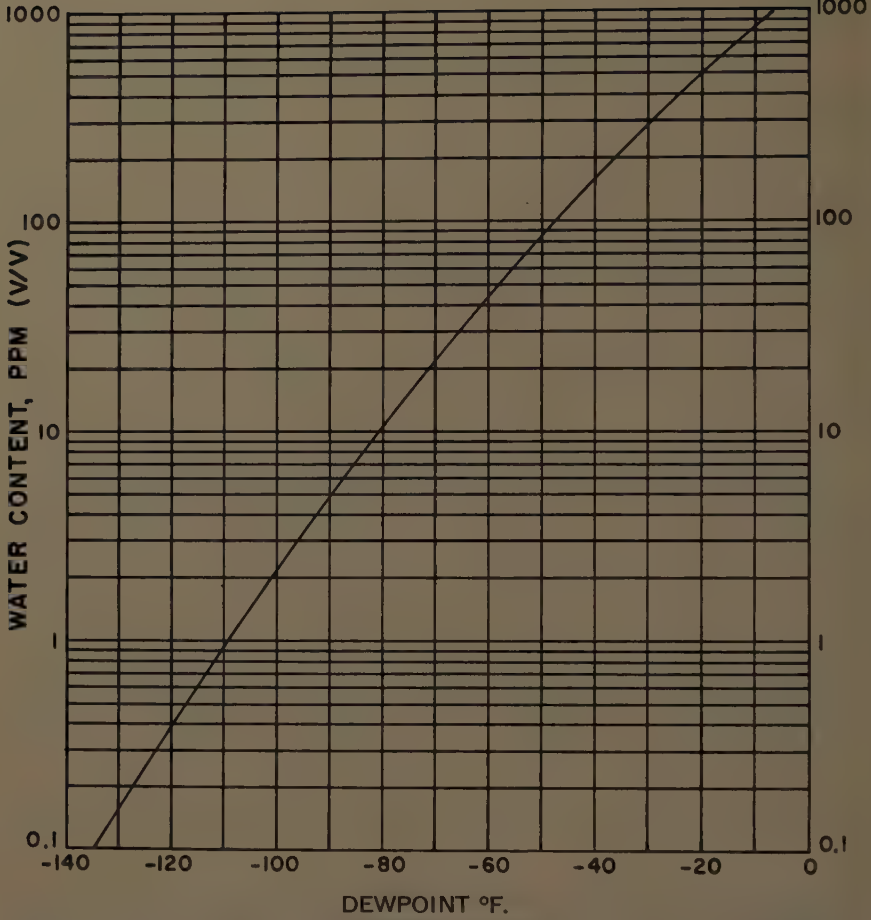


FIGURE 1. Water content, parts per million (by volume over ice) versus dewpoint temperature at atmospheric pressure (14.7 psi).

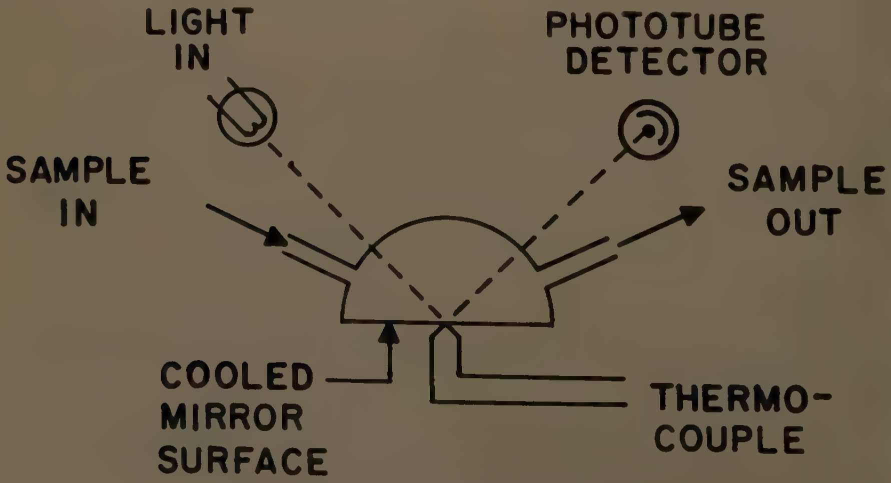


FIGURE 2. Dewpoint photoelectric detector.

passing into the sample cell thermostats the reference liquid. Incident light will be reflected by changes of the refractive index of the sample composition.

Water and water vapor absorb light in the near infrared spectrum, and suitable infrared analyzers may be used for detecting the concentration of moisture in a liquid or gas system. In this system it is important that interfering materials, which tend to absorb infrared radiation in the same region as moisture, be absent from the system.

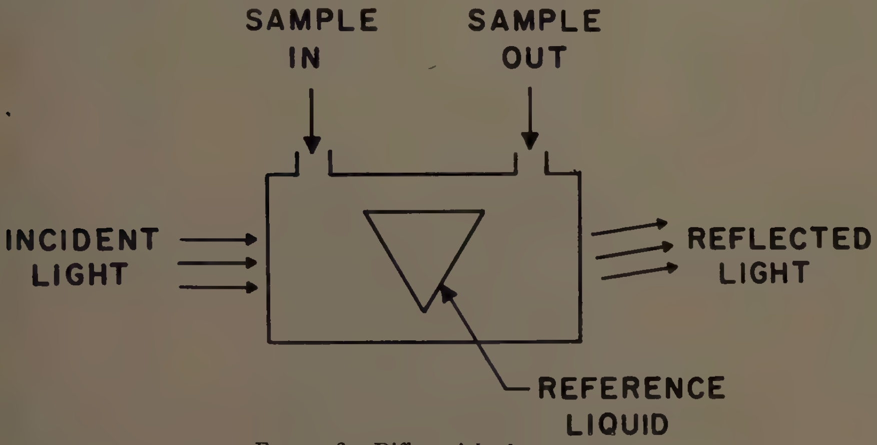


FIGURE 3. Differential refractometer.

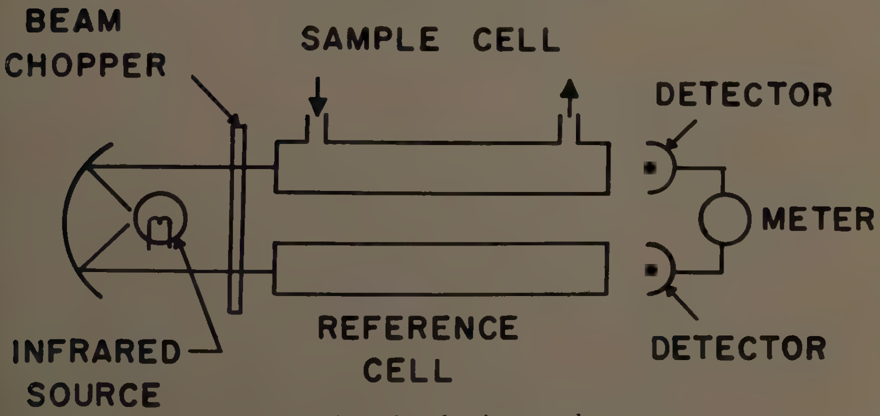


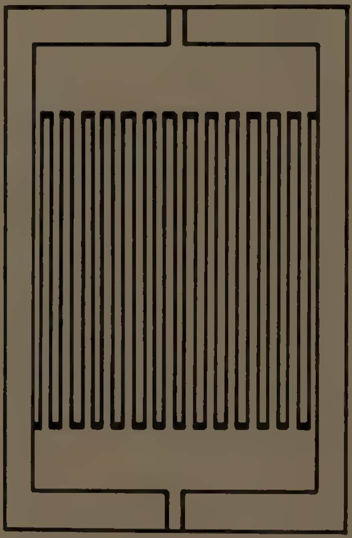
FIGURE 4. Infrared moisture analyzer.

FIGURE 4 shows the optical schematic of a process infrared analyzer. This type of infrared analyzer, used for moisture measurements, is the nondispersive type that compares the infrared absorption of a known reference sample against a plant stream sample.

A source of infrared radiation is passed through a sample cell and reference cell. A suitable detector, or pair of detectors, may be used to measure the differences in the infrared absorption as a function of concentration between the known mixture of constant composition and the sample.

Electrical moisture-measuring instruments include those that measure resistance, conductance or inductance, dielectric or power factor, or coulometric current.

Certain types of hydroscopic salts may be used for measuring changes in the resistance or conductance of a nonconducting film as a function of the change of water-vapor concentration. The hydroscopic materials may be either salts dissolved in a water-soluble film, acidic hydroscopic films, or sulfonated plastics. The hydroscopic film or coating is placed over a bifilar winding or etched grid (FIGURE 5).



MOISTURE
GRID

FIGURE 5. Etched moisture grid.

Changes in relative humidity as a function of resistance (FIGURE 6) or conductance may be made. An AC voltage is applied to the two electrodes to prevent electrolysis of the moisture. The changes in resistance, current, or conductance as a function or relative humidity is measured. This electrical change is directly proportional to the moisture absorbed and desorbed on the hydroscopic coating.

Dielectric and power factor instruments can measure electrical changes in a system as a function of water concentration. This measurement is very sensitive, but it is subject to changes in bulk density, uniformity, and other materials present in the system. These instruments must be calibrated against materials of known moisture concentration.

The conductance, inductance, or capacitance instruments measure electrical changes as a function of water concentration. Instruments of this type are used for measurement of materials that have small variations in moisture concentration. Samples must be fairly homogeneous in composition.

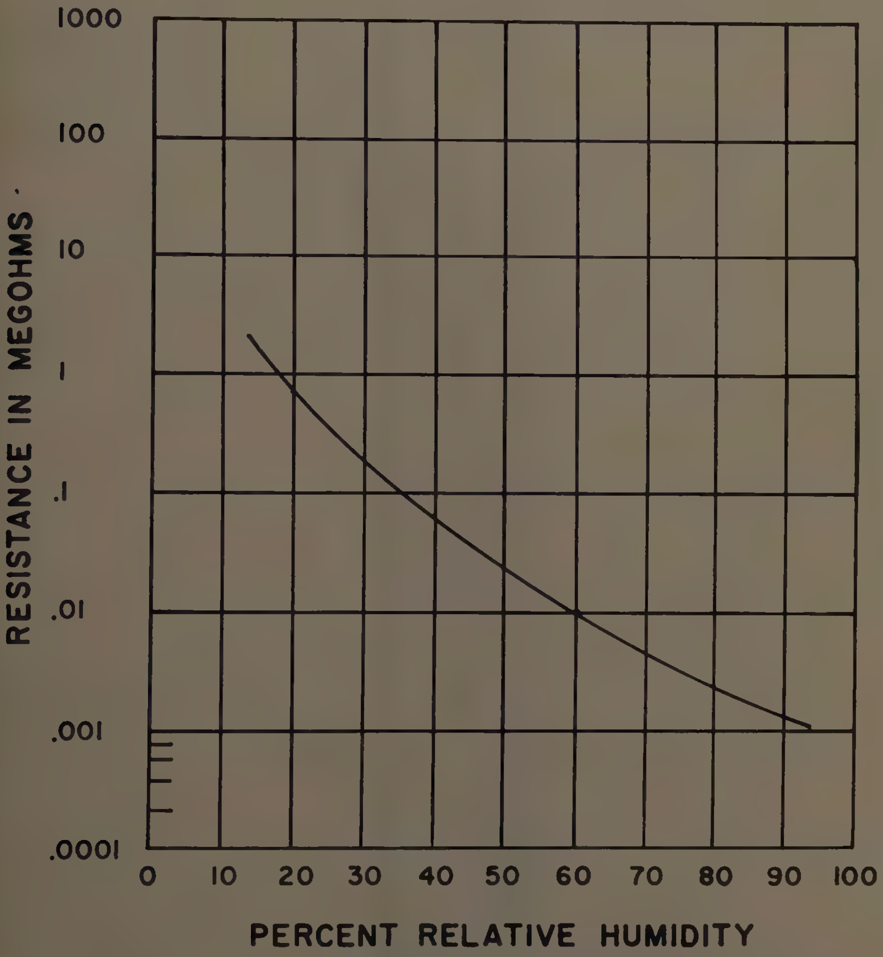


FIGURE 6. Change in resistance versus per cent relative humidity of air.

Coulometric moisture-measurement instruments are based on the electrolytic decomposition of moisture absorbed on an appropriate desiccant film through which gas flows at a predetermined and controlled rate. The current that results from electrolysis is quantitatively related to the moisture in the system. The sensing element consists of a pair of bifilar electrodes that are helical-wound and closely spaced.

The electrodes are placed in an inert flexible tubing that is coiled into a cell housing. Efficient desiccants are used to coat the electrodes. FIGURE 7 shows a cross section of a typical electrolysis cell.

A system containing water vapor is passed through the cell at a given and controlled flow rate. The initial reaction in the cell is complete absorption of moisture from the other gases. A DC voltage is continuously applied to the electrodes that electrolyzes the absorbed water into hydrogen and oxygen. The current resulting from the electrolysis is directly proportional to the moisture in the system. A typical flow schematic of the coulometric analyzer is given in FIGURE 8.

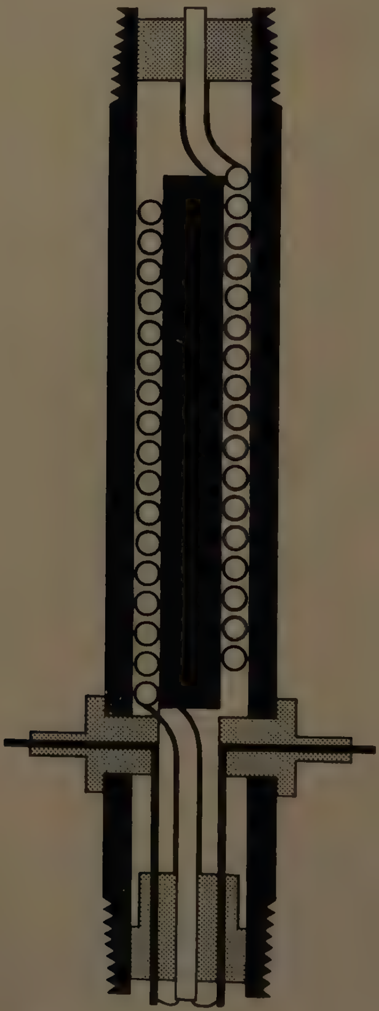


FIGURE 7. Coulometric electrolysis cell.

Thermal-moisture instruments measure the heat of absorption of moisture

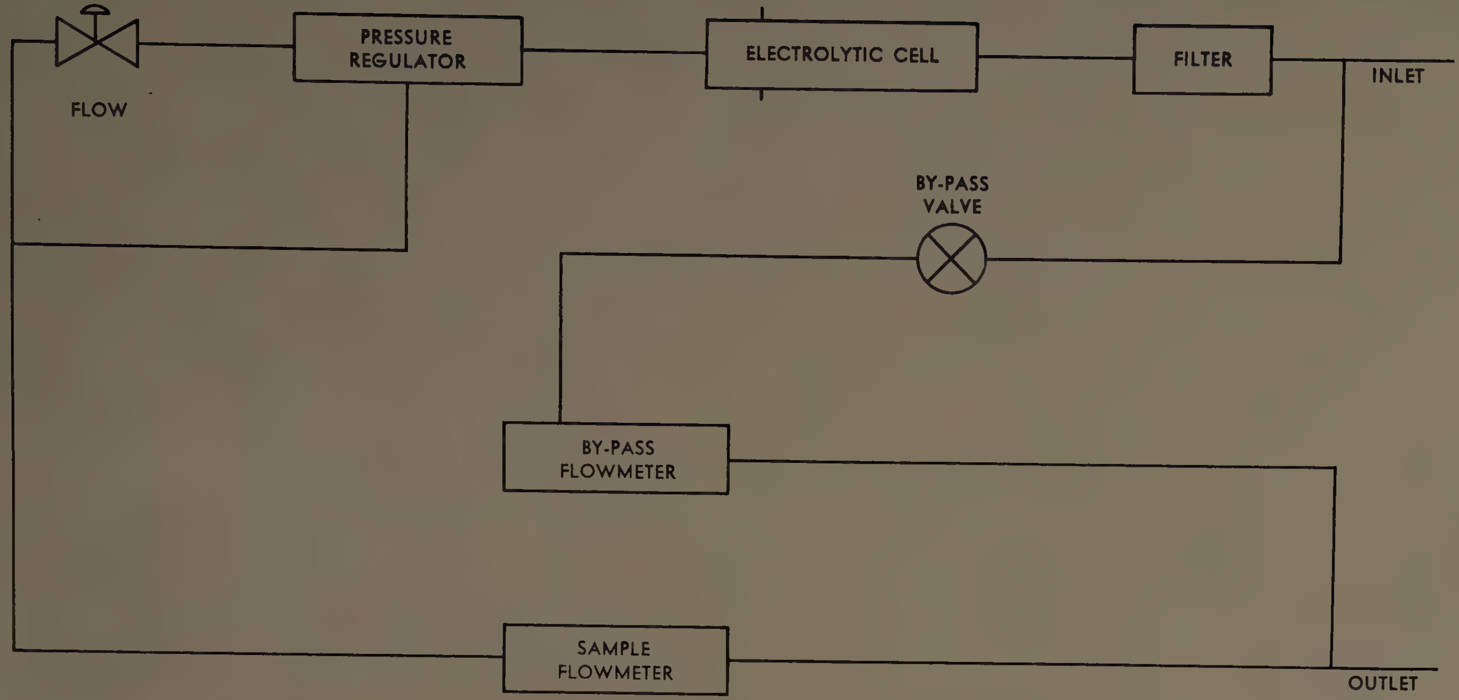


FIGURE 8. Flow system for coulometric moisture analyzer.

on a desiccant or the change in thermal conductivity of water vapor in a gas system. The heat of absorption of moisture on a desiccant that is in contact with a sensitive temperature device may be used for measurement of the amount of moisture in a system by measurement of the rise in temperature.

Although moisture is an interfering material in many types of gas chromatography and gas thermal conductivity systems, special types of gas chromatography columns and detectors have been used for measurement of moisture in gases.

Nuclear instruments may be used to measure moisture in solids when the density of the material is known. The moisture detector is based on having a neutron source and an appropriate detector for measuring the amount of neutron absorption due to moisture changes. The effect of bulk density is significant, and measurement in density changes must accompany moisture changes for a given system.

AUTOMATIC ANALYSES AS APPLIED TO WATER QUALITY DETERMINATIONS AND WATER TREATMENT

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Introduction

The objectives of this paper are to present current information on the applications of automatic analytic instruments to the evaluation of pertinent characteristics of surface waters and the monitoring of water treatment processes.

There are two objectives in the automatic monitoring of surface waters: first, the collection of basic data on the biological and chemical characteristics of a river for comparative studies, particularly in terms of permissible loading of oxygen-consuming pollutants; second, provision for automatic surveillance with appropriate circuitry to provide warning and sample collection when the norms of certain parameters are exceeded.

A modern approach to the assembly of basic data for water quality on a national scale presented in 1958 by Palange and Megregian[1] includes a broad coverage of manually collected samples and analyses for biological, chemical, and radiological parameters. This program is detailed in a recent report of the Public Health Service.[2]

For the field biologist, this approach has the added advantage of providing quantitative information on the productivity of a body of water in terms of the numbers and diversity of the various successions of organisms. This sequential dependence is customarily called a "food chain," and many unicellular and multicellular organisms are involved. For all of them the ultimate energy source is due to photosynthesis, that is the conversion of radiant energy of sunlight into stored chemical energy by floating algae and rooted aquatic plants. Thus the alteration of any critical environmental factor, whether the alteration is natural or man-made, is evident by its effects upon various members of the food chain.

For most of the diagnostic parameters, my associates and I now have suitable instrumentation that permits correlation of automatically recorded data with the biological findings. In 1956, however, such organized instrumentation did not, to our knowledge, exist. In March 1957, we proposed a research program on automatic monitoring of water quality to INCODEL (Interstate Commission on the Delaware River Basin). Within one month this program was started with an awareness of certain existing instrumentation and also of certain desirable parameters for which, at that time, no suitable or dependable sensing instruments were available.

The INCODEL Monitor Program

The initial INCODEL system was planned with instruments for the automatic recording of temperature, conductivity, hydrogen-ion concentration, and oxygen concentration. For the first three items, there existed dependable detecting and recording instruments that could be adapted to our needs.

The problems of oxygen measurement were very complex, and considerable research was pursued by the Lehigh group on dependable methods. It is sufficient here to record that there were two promising methods. The first involved the paramagnetic and/or thermal-conductivity detecting element for a gas mixture containing oxygen. The gas mixture was derived by scrubbing an oxygen-containing water sample with nitrogen and submitting the gaseous mixture to analysis. The original concept of this method was developed at the Taft Center in Cincinnati, Ohio by Levine *et al.*[3] A commercial version, reported by Dixon at the Water Quality Symposium,[4] is now under test in the lower Delaware River.

The alternate promising method involved polarographic principles. The first dependable automatic polarographic oxygen-measuring instrument was reported by British workers[5] on a revised dropping-mercury electrode. This design avoided certain mechanical and hydraulic objections of the conventional mercury electrode for which references are legion and for which the principles are set forth in the fundamental paper by Heyrovsky.[6]

The Lehigh group developed a dependable dropping mercury electrode, which included temperature compensation;[7] however, we found that this electrode was unreliable in water of conductivity below 200 microhms. As the upper Delaware River shows conductivities below 40 microhms, it was evident that an ionized-salt feed to the electrode system was required. This was added, including constant head devices for regulated flow of water, mercury, and salt solution. The resultant was a complex of instrumentation that worked but required frequent calibration. It was evident that our proposed weekly maintenance, chart changing, and sampling routine would be too infrequent to provide adequate calibration of this mercury electrode.

The timely development by Carritt and Kanwisher[8,9] of a new polarographic oxygen electrode solved this conductivity problem and, as described below, presented two additional difficulties. However, we adopted this electrode system that uses platinum as the indifferent electrode, against a sacrificial electrode of silver-silver oxide in 0.5 N potassium hydroxide. The key feature is the containment of the alkaline electrolyte within a thin polyethylene film highly permeable to molecular oxygen. This arrangement protects the platinum surface from metallic deposition or incidental fouling that has prevented the use of the rotating platinum electrode in waters of variable composition and pollutional load. Various modifications of the rotating electrode are presented in our previous paper.[7] However, reference should be made to a recent German electrode system,[10] using a noble and a base metal, in which mechanical polishing maintains a clean and uniform area for each electrode of the rotating assembly. We have not investigated this electrode.

As noted by Carritt and Kanwisher,[8,9] we have observed the sensitivity of the Carritt electrode to flow rate and to temperature variation. We have also added the "Morris Phenomenon," that is, the marked sensitivity of this electrode to incident light. Appropriate minimal flow rate and exclusion of light remove two of the difficulties. We have investigated four methods of temperature compensation.

The first and obvious method involves the use of thermistors. Unfortunately no presently available thermistor of United States design, in the 2000- to 3000-ohm shunting range, has better than a 4.8 per cent change in resistance per degree centigrade. The published information, studies at the Taft Center, and our investigations all indicate the need for about 6 per cent change per degree centigrade. For our operating automatic monitor system on the Delaware River, we are at present using special Western Electric thermistors with a resistance change of 4.4 per cent per 1° C. We therefore calibrate our oxygen electrode at frequent intervals. One of the three remaining methods shows, at present, particular promise, and we plan to develop it.

For the measurement of river turbidity, it was our original plan to use a transmission type turbidimeter. We rejected this for several reasons[7] and were pleased to find, with the cooperation of the ORSANCO (Ohio River Valley Sanitation Commission) group, a new reflectance turbidimeter.* This was reported at length by Hach[11] at the Symposium on Water Quality Measurement and Instrumentation. The Hach reflectance-principle turbidimeter was installed at our pilot facility at Riegelsville, N.J.[7,14] in November 1959. Maintenance and calibration are reported in our previous paper[14] presented at the Taft Center. For the present paper, we report only that the reflectance-type turbidimeter uses 6 serially connected selenium photocells mounted peripherally to a constant-intensity light source. This assembly is contained within a tube 6 inches in diameter and 4 feet in length through which water flows. The internal walls are flat black and, for waters of negligible turbidity, there is a negligible back reflection to the photocells. We have developed appropriate calibrations for the photocell-millivolt output in terms of turbidity as measured by the standard Jackson Candle turbidimeter.

It is noteworthy that turbidity in terms of the Jackson Candle Standard rarely exceeds 400 u. in rivers of the eastern United States. In contrast, Schaible[15] reports variations in turbidity in the Illinois River, in the period 1941 through 1959, which range from a minimum of less than 10 u. in 1947 and 1948 to a maximum exceeding 5000 u. in 1947, 1948, and 1950. Such high concentrations of suspended solids would yield a very nonlinear response in the reflectance turbidimeter and would produce negligible response in a transmission turbidimeter. In addition, excessive deposition would occur on the glass walls of the cuvette in the transmission instrument.

As previously implied, oxygen derived as a by-product of the photosynthetic reaction supplements the oxygen concentration in water due to equilibrium with atmospheric oxygen. For example water at 20° C. and at air equilibrium will contain 9.2 oxygen ppm. At 0° C. the corresponding value is 14.6 ppm. It is evident that the intensity of sunlight determines the rate of oxygen liberation from chlorophyll-containing plants. This supplemental oxygen aids in the stabilization of organic pollutants in water. It is thus desirable to measure sunlight intensity as part of the basic data program and as an interpretive criterion in automatic surveillance. We experimented with various types of photovoltaic cells for measurement of solar radiation. The inadequacies of this approach are set forth in our previous report.[7]

We therefore selected the standard Eppley Pyrheliometer for measurement of sunlight in terms of the solar constant, that is, gram-calories per square centimeter per minute. This international standard is applicable elsewhere as each Eppley instrument has been intercompared with the Smithsonian and United States Weather Bureau instruments. The Pyrheliometer consists of a multiple junction thermocouple assembly using platinum and rhodium, and the output approximates 2 mv./gm. cal./sq. cm./min. An appropriate potentiometer provides a calibrated output into a linear-recording potentiometer of sufficient input impedance to minimize load on the thermocouple assembly.

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* It is appropriate here to give due credit to the extensive work on water quality monitoring by personnel of ORSANCO.[12,13]

One of these instruments at our pilot monitor station has been recording sunlight since December 1959. A preliminary examination of our data shows an expected significant seasonal correlation between oxygen concentration and sunlight intensity and to a lesser extent the modulating effect of this relation by river turbidity. This latter effect is in large measure due to the altered light penetration of turbid water with consequent reduced photosynthesis.

At the Riegelsville station the instrumentation is contained in a heated weatherproof building, and water is delivered to the sensing elements in the building from a floating pump assembly in the river. Insulation and a heating cable protect the piping against freezing. A surge tank provides adequate storage for automatic sampling via a solenoid valve circuit.

We are now constructing two additional monitor stations on the Delaware River: one at Montague, N.J. and one at Martins Creek, Pa. Each of these stations, with improved equipment, will record the 6 variables previously described. We presently plan an 11-station network[16] of monitor stations from the headwaters of the Delaware River at Hancock, N.Y. down to Trenton, N.J. Included in the plans are tentative specifications for telemetering all data to a central office in Philadelphia.

Instrumental Analyses Applicable to Municipal and Industrial Water Supply

There are many additional analytical methods applicable generally or for special needs in a particular industrial usage.[17-19]

Automatic titrimetric methods are in use for total hardness,[11,20] methyl orange and phenolphthalein alkalinity,[11] and fluoride ion.[11] All of these are dependent upon a colorimetric end point. If desirable, phosphate ion, sulfate ion, chloride ion, ammonia, ferric ion, and carbon dioxide could be similarly determined. Alternately chloride ion may be determined by the silver-silver chloride electrode reported by Noebels.[21] Carbon dioxide may also be determined by the special *p*H-sensitive electrode reported by Severinghaus.[22]

One interesting amperometric method for measuring residual chlorine has been reported by Jones and Joyce.[23] This is a desirable control device to assure adequate chlorine residual in water-treatment plants. In such plants automatic *p*H recording and control are valuable in reduction of corrosion and in optimum flocculation.[24] Turbidity measurement would be applicable here if desired. The development of an automatic instrument for the measurement of surface tension[25] provides for monitoring of water subject to contamination by synthetic detergents. One large filter plant (Philadelphia, 150 M. G. D.) is installing automatic monitoring for gross radioactivity of intake water.

Boiler Feed Water and Condensate

In the present development of very high pressure boilers (up to 5000 psi.) analytical methods have assumed greater importance in the chemical and physical evaluation of both boiler feed water and boiler condensate. An excellent review of instrumental needs in steam-electric stations is presented by Crandall.[26] For feed water, removal of CO_2, O_2, and NH_3 are customarily achieved in deaeration equipment. A variety of analyses, all actually or potentially instrumented, may serve to evaluate and modulate the composition of input water. The following is a minimal list: silicon dioxide, total hardness, phosphate, hydrogen ion concentration, chloride ion, and conductivity.

Instrumental measurements of these variables will serve to control, for example, water-softening and silica-reduction processes. These in turn may be used to reduce boiler blowdown to a minimum.

As boiler condensate is essentially distilled water, the contaminants exist in the parts-per-billion range.

Several of these contaminants are highly deleterious and some are indicative of boiler malfunction.

Oxygen is highly corrosive, and at least three automatic methods for determination and control in the range 0 to 30 ppb are in use. The first two methods depend upon a change in conductivity in the condensate sample. In one method[27] metallic thallium is in contact with the condensate and the resulting thallium hydroxide increases the conductivity in proportion to the oxygen concentration. In the other method[21] nitric oxide is equilibrated with the condensate. The resulting nitrous acid raises the conductivity proportionally in the range 0 to 25 ppb. The third method[20] is dependent upon the color change of indigo carmine in the presence of trace amounts of oxygen. Hydrazine, a deoxygenator, can be measured colorimetrically in condensate by the specific yellow color[18] developed in the reaction with *p*-dimethylaminobenzaldehyde.

Hydrogen is also a factor in corrosion of boilers, and in certain nuclear plants it is deliberately introduced to suppress the dissociation of water. An instrumental method for continuous monitoring of hydrogen[18] is in use. The basic principle is measuring the comparative thermal conductivities of a mixture of water vapor, hydrogen, and air against a mixture of air and water vapor.

The presence of certain ions in condensate is indicative of contamination by "carry-over." Automatic measurement of hydrogen ion, phosphate ion, or specific conductivity are diagnostic.

Silica presents a special problem because this oxide is deposited in an insoluble form upon turbine blades and reduces the efficiency of the turbine. Two automatic methods for silicon dioxide in the range 0 to 50 ppb[28] are used. Both are based upon the color developed by reaction with ammonium molybdate.

For very high purity steam, conductivity measurement has only limited value and has been replaced by a flame photometer[26] reported to detect sodium ion at the level of 0.1 ppb.

Instrumental Analyses Applicable to Waste Disposal Systems

In the monitoring of industrial waste discharges, three constituents are of major importance. Cyanides are highly toxic and are contained in wastes from steel making and electroplating. Much has been done on the development of an automatic method for cyanide, but in the present state of the technique much remains to be done, as noted by Freeman.[29]

Phenol, a constituent of coke plant wastes is toxic and imparts a strong objectionable taste and odor to chlorinated waters. Instrumental methods have been developed but, at present, Freeman's observations are valid. Hexavalent chromium from electroplating is very toxic. Customarily this is reduced and precipitated in the trivalent state. An automatic colorimetric method has been reported.[23]

Oxidation-reduction potential measurement in millivolts is applicable in wastes low in oxygen[23] and is particularly sensitive to oxidants such as hexavalent chromium. Residual chlorine, recorded and controlled, is obviously applicable to effluents from waste disposal systems. A final "spectacular" is the automatic method for measurement of chemical oxygen demand.[30] This is discussed by G. Cohn elsewhere in this monograph.

It is clear that there are many methods, existing and potential, for evaluation of physical and chemical characteristics of water. These are applicable to a variety of water uses and can be tailored as to precision required and altered for level of sensitivity. Their applications are, in large measure, contingent upon their economic justification.

In conclusion it is pertinent to quote part of a recent editorial: "The day is coming when we will have to manage water quality of whole river basins, much in the same push-button manner that we now transmit and manage electrical power. Certain streams will be fully instrumented. Data will be telemetered. A central computer will turn out the finished data. . . . Our successors will then look back to the good years of the 1960s when things were rather simple.[11, 31]"

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AUTOMATIC ANALYSIS OF ATMOSPHERES

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The development of automatic analyzers for air and other atmospheres has followed several routes. The two most easily discernible paths of development have been the evolution of equipment originally designed for spot testing of atmospheres in potentially hazardous areas and the adaptation laboratory instruments to continuous process applications. Only comparatively recently has there been a general trend toward development of instrumentation with the process application as the objective at the outset of the project.

Present-day requirements of industry make desirable the possibility of monitoring the concentration of almost any gas in any background stream or mixture of gases. Concentrations of interest range all the way from a few parts per billion to 100 per cent of the compound measured. In some applications it is desirable to analyze for more than one compound in the same stream. Temperatures and pressures of the sampled atmospheres can vary widely. All such requirements influence the choice of method and equipment selected to do a particular job.

Many physical and chemical principles are now employed or are under consideration as a basis for automatic atmosphere analyzers. The following list includes physical, chemical, and electrochemical techniques:

Detection Principles Employed

The detection principles in use are the following:

(1) Measurement of heat produced by catalytic combustion: (a) on heated wire filaments, (b) in granular catalyst beds, and (c) on catalyst coated surfaces.

(2) Measurement of heat transfer in a gas sample: (a) by thermal conduction, (b) by convection, and (c) by differential measurements of (a) and (b).

(3) Measurement of radiant energy absorbed in the air or gas sample or in a liquid scrubber: (a) infrared, (b) ultraviolet, (c) visible, (d) microwave, and (e) radioactive (alpha, beta, thermal neutrons).

(4) Ionization phenomena: (a) ion pair production, (b) ion recombination rate, (c) ion removal by contaminants, (d) ion mobility, and (e) electron affinity.

(5) Electrochemical measurements: (a) potentiometric-concentration cells, (b) conductivity cells, (c) coulometric generation of reagent to maintain preselected concentration level, (d) polarography, and (e) electrode depolarization.

(6) Gas and vapor chromatography: (a) adsorption chromatography, and (b) partition chromatography.

(7) Chemical colorimetric measurements: (a) sensitive reagents dispersed on moving plastic or paper tapes, (b) liquids exhibiting color response to specific gases, and (c) production or inhibition of fluorescence.

(8) Magnetic properties: (a) differential cooling of heated filaments due to

magnetic field influence on paramagnetic gases, (b) mechanical displacement of a dimagnetic sensor by paramagnetic gas under the influence of a magnetic field, and (c) differential pressure between two volumes of gas created by the effect of a varying nonuniform magnetic field on a paramagnetic component of the gas mixture.

(9) Solid state phenomena: (a) effect of gases and vapors on work function of surfaces, (b) effect on contact potentials, and (c) electron transfer at semiconductor junctions.

Because it will not be possible to discuss each of these principles in detail, a selection of those in general use or having a potential for wide applicability has been made.

Instruments that apply single physical principles to analyses do not generally identify and measure single constituents, but identify classes or merely indicate changes in the composition of the atmosphere. Where constituents likely to be present are known or limited, this information can quite often be interpreted in terms of composition, but if identification where similar materials are present is required, it may be necessary to employ a combination of principles or to use a much more complex instrument.

Chemical principles offer the advantage of specificity but are often unsuitable for continuous duty automatic analyzers because of the need to supply reagents and dispose of wastes.

Measurement of Combustibles by Catalytic Hot Wire Analyzers

The catalytic hot wire filament was first employed as a means of evaluating explosive hazard, and it has enjoyed widespread acceptance over a period of about 25 years. Analyzers of this type operate by measuring the increase in temperature of a filament as it catalyzes the combustion of the flammable vapor surrounding it. The minimum concentration of combustible gas or vapor in air that constitutes an explosive hazard varies from compound to compound, but it has been found that the lower explosive limit (LEL) can be roughly defined in terms of the calorific value of the compound; thus such a unit will give an approximate indication of explosibility for all compounds without need for individual calibration. With calibration for specific compounds, these units can be used in solvent recovery processes, drying ovens in enameling plants, acetate spinning mills, and similar process-control applications.

FIGURE 1 is a schematic diagram of a simple portable gas detector of the hot-wire type. The catalytic filament is made one arm of a Wheatstone bridge and is heated to a preselected temperature by the passage of a controlled electric current from the battery power source. The bridge is balanced on fresh air, and then the atmosphere to be tested is drawn into the chamber surrounding the filament. Heat produced by burning of any combustible gas present raises the filament temperature, increasing its resistance and unbalancing the bridge. The bridge unbalance is indicated by the galvanometer which is calibrated in terms of percentage of the lower explosive limit or in percentage by volume of the compound of interest.

When it is desirable to continuously monitor an area for the presence of combustible gases or to analyze a process gas stream, these instruments are equipped with motor-driven sample pumps, sample gathering systems, and similar accessories and are powered from the building 115 to 230 volt system. FIGURE 2 shows an installation of this type of equipment in a pumping station on a transcontinental pipe line.

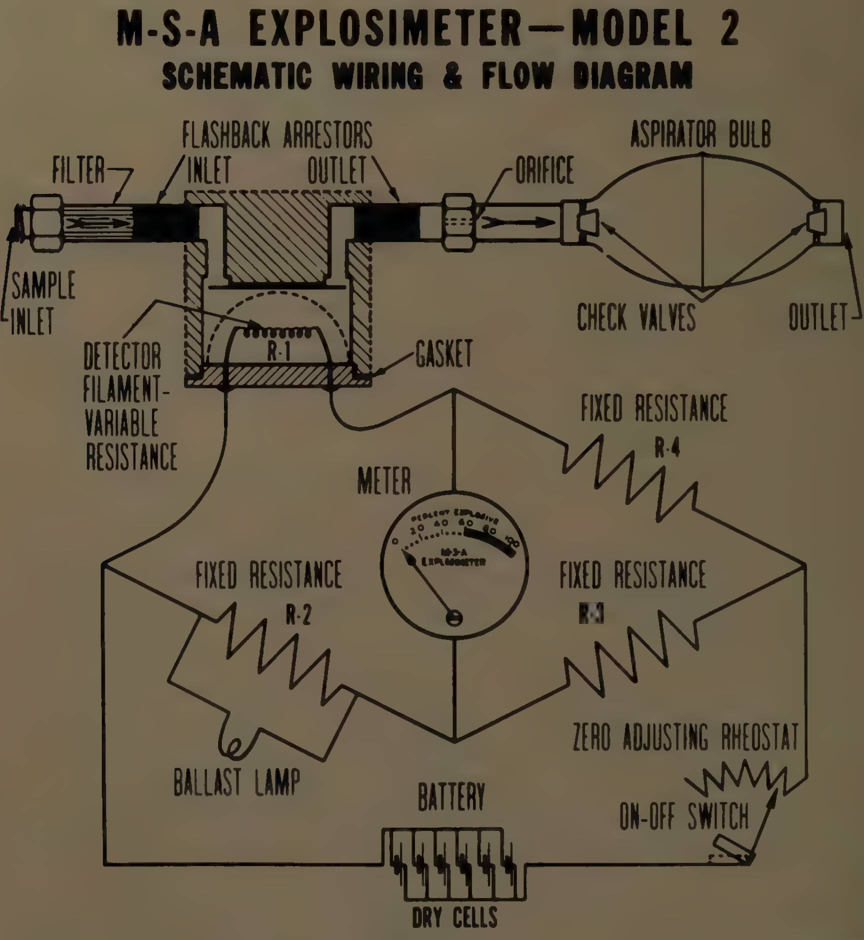


FIGURE 1.

Heat of Combustion in Granular Catalyst Beds

In the late 1920s and early 1930s an instrument was developed for measuring toxic concentrations of carbon monoxide in the air by measuring the heat evolved by burning the CO on a very active catalyst. This was one of the earliest instruments designed specifically as an automatic atmosphere analyzer, and many similar instruments are still being put into service each year.

FIGURE 3 is a schematic diagram of the detector cell. In this design the

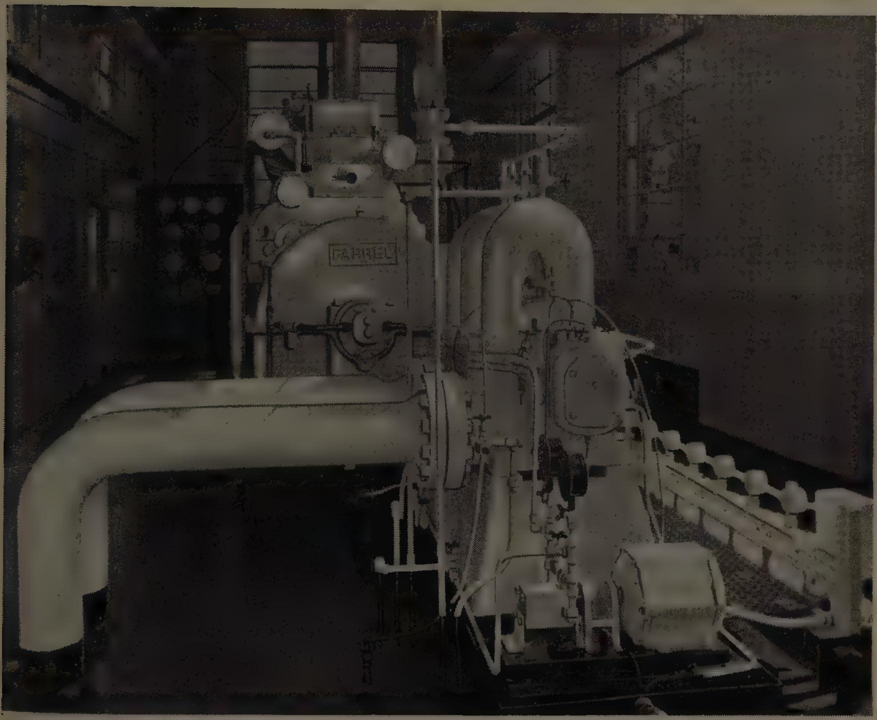


FIGURE 2.

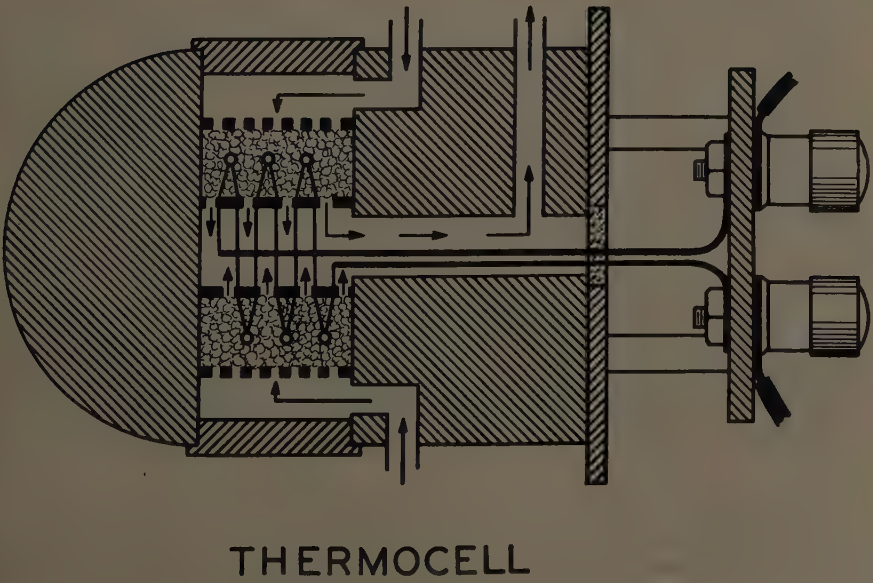
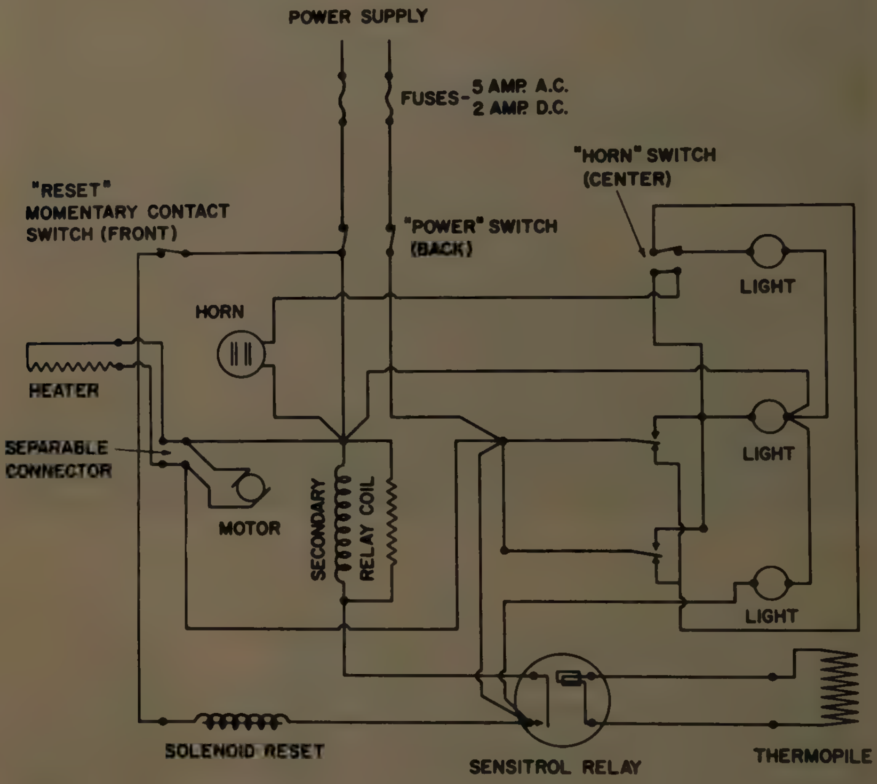


FIGURE 3.

sample is drawn simultaneously over active and inactive beds. The temperature differential resulting from combustion in the active bed is picked up by the thermopile. All other temperature variations affect both junctions equally.

FIGURE 4 shows in diagrammatic form the essential components of a continuously operating instrument. The emf generated by the thermopile can be used to drive a recorder, alarm relay, or ventilation controller as desired. FIGURES 5 and 6 show a panel installation of this type of equipment as used to monitor the air in vehicular tunnels. The first installation of this type was in the Holland Tunnels, New York, N.Y.



WIRING DIAGRAM

FIGURE 4.

Infrared Spectroscopy

Radiation in the 2 to 15 μ region of the spectrum has proved very useful in spectrographic identification of materials. Spectrographs of the dispersive type, which continuously vary the wave length by means of a prism or grating

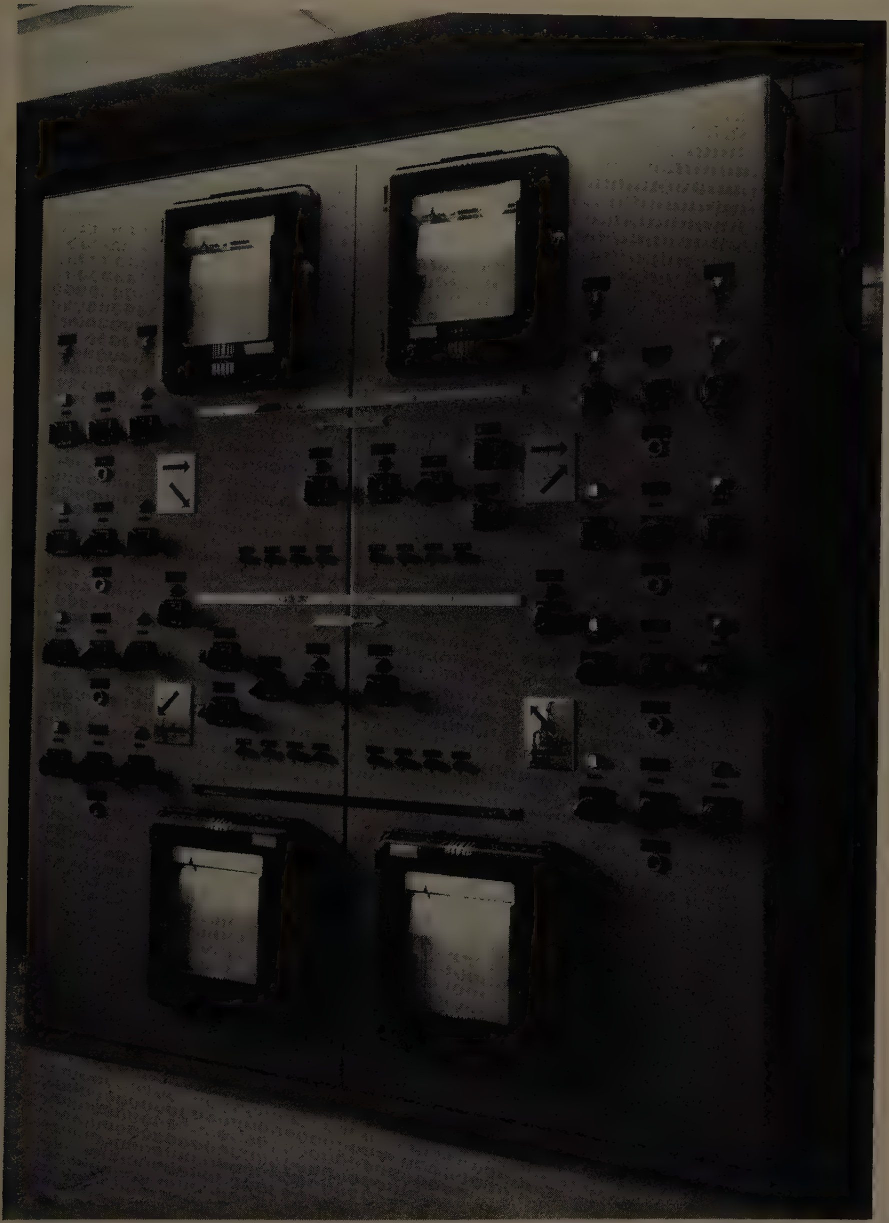


FIGURE 5.

can produce a spectrogram in this region that can serve as an identifying fingerprint for a particular material. A spectrogram, however, is a complex presentation of adsorption versus wave length, and identification must be made by comparison to spectrograms of known samples. Although this analysis technique is extremely useful in the laboratory, it is not well suited to continuous automatic analysis.

A somewhat simpler and more sensitive version of the infrared analyzer is the nondispersive type, which does not produce a spectrogram but effectively umps the infrared radiation, measuring the total change in absorption. Instruments of this type can be sensitized or made specific to the desired compound by variation in choice of transmitting windows, filters, and the detector fill.

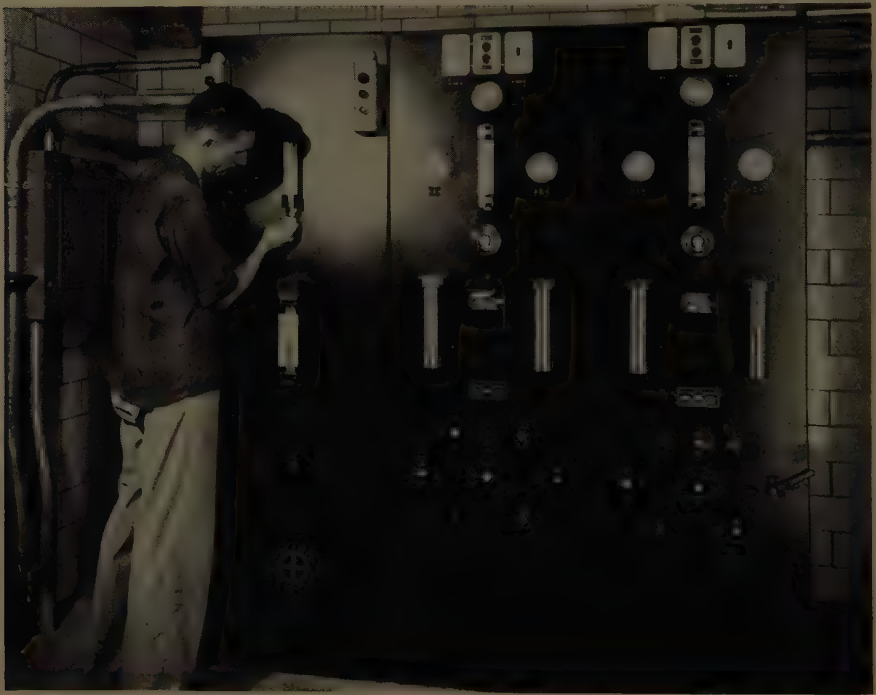
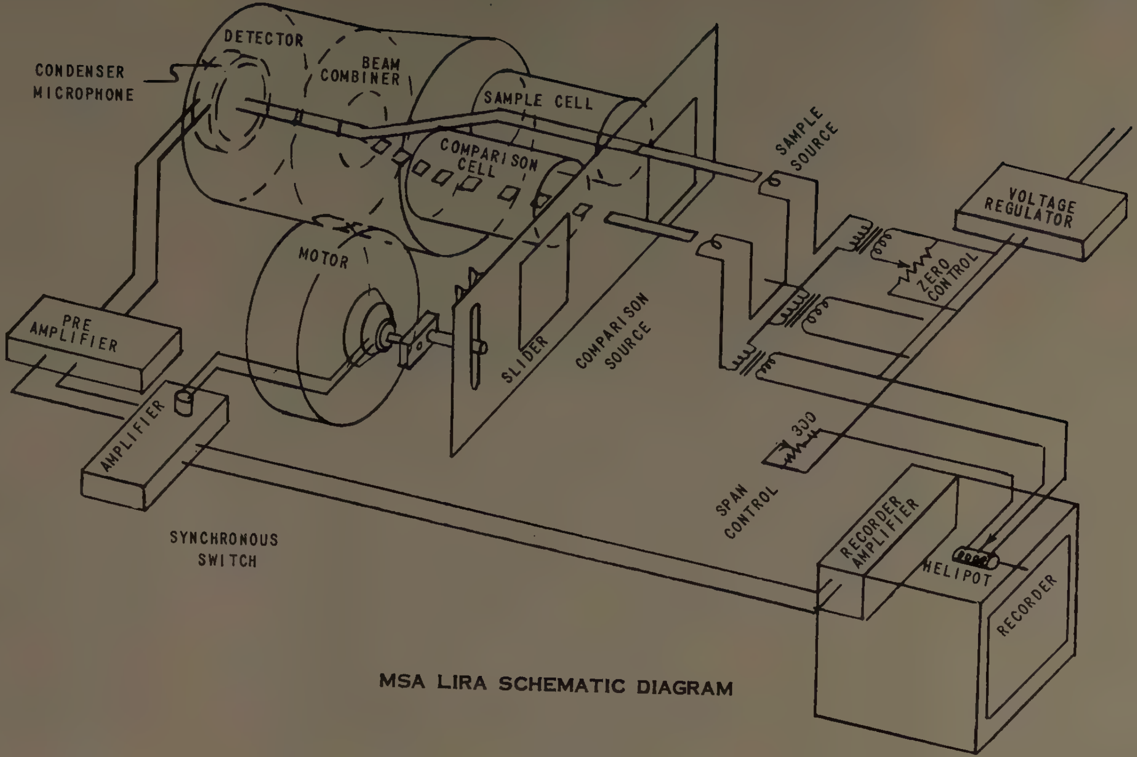


FIGURE 6.

FIGURE 7 shows diagrammatically the operation of the nondispersion type of analyzer. The detector is filled with a dilute concentration of the gas of interest in a noninfrared-absorbing diluent. The detector gas mixture therefore absorbs energy in exactly the same portions of the spectrum as those influenced by the detected contaminant when it is present in the sample cell. Radiation from two infrared sources is made to traverse separate paths and enter a common detector cell. Sample and comparison cells are provided so that the beams are caused to pass through the tested sample and a reference



MSA LIRA SCHEMATIC DIAGRAM

FIGURE 7.

gas. For atmosphere monitoring, the reference is clean air. In process-control applications the reference may be the background gas mixture. The beams are interrupted alternately at a fixed frequency. When the sampled atmosphere is free of the contaminant, equal radiation reaches the detector and a steady energy level exists. When the contaminant is drawn into the sample cell, the energy reaching the detector from one beam is attenuated. The gas in the detector therefore heats and cools at the frequency of the beam interruptions. Resultant expansion and contraction of the detector gas fill causes movement of a metal diaphragm that is one plate of a capacitor in an electronic oscillator circuit. The varying capacity is converted to an electric signal to drive a meter, recorder, or alarm relay.

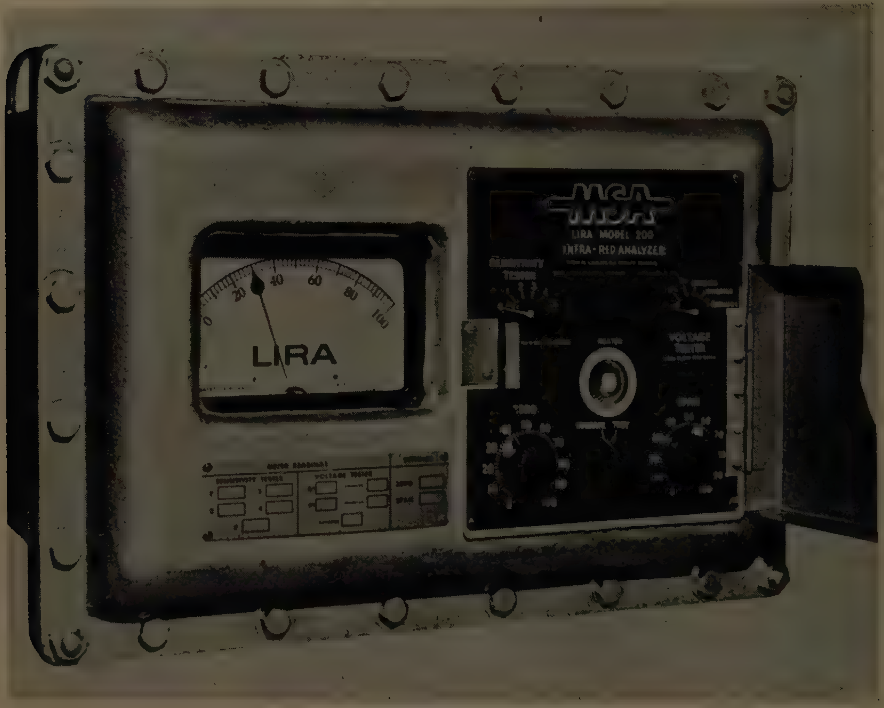


FIGURE 8.

Sensitivity of nondispersion infrared analyzers can range from about 100 ppm to high percentage concentrations. Applicability to detection of toxic air contaminants is limited to those with strong absorption bands and relatively high MAC values. Explosive hazard detection is easily achieved, and the instrument principle is very desirable when the kind of combustible gas likely to be present is known. Individual instruments lack the universal response which makes the catalytic hot-wire detectors so useful as survey or general surveillance monitors.

FIGURES 8 and 9 show explosion-proof and nonexplosion-proof examples of infrared instruments designed for fixed installations. Figures 10 and 11 show a mobile survey vehicle equipped with similar equipment. The instrument shown in figure 12 is portable and draws its power from the standard 115-volt house supply.

Ultraviolet Spectrophotometry

Many compounds are opaque to certain wave lengths of ultraviolet radiation. This fact is used in the design of photometers that measure the concentration of the compounds in the air by the amount of attenuation a beam of UV radiation suffers in traversing a fixed path length. Analyzers of this type are often similar to the infrared photometers described above except that the energy source is a mercury vapor lamp and phototubes are used for detectors. Such instruments find applications in monitoring the air or process streams for mercury vapor, chlorinated solvents, carbon disulfide, and many other compounds.

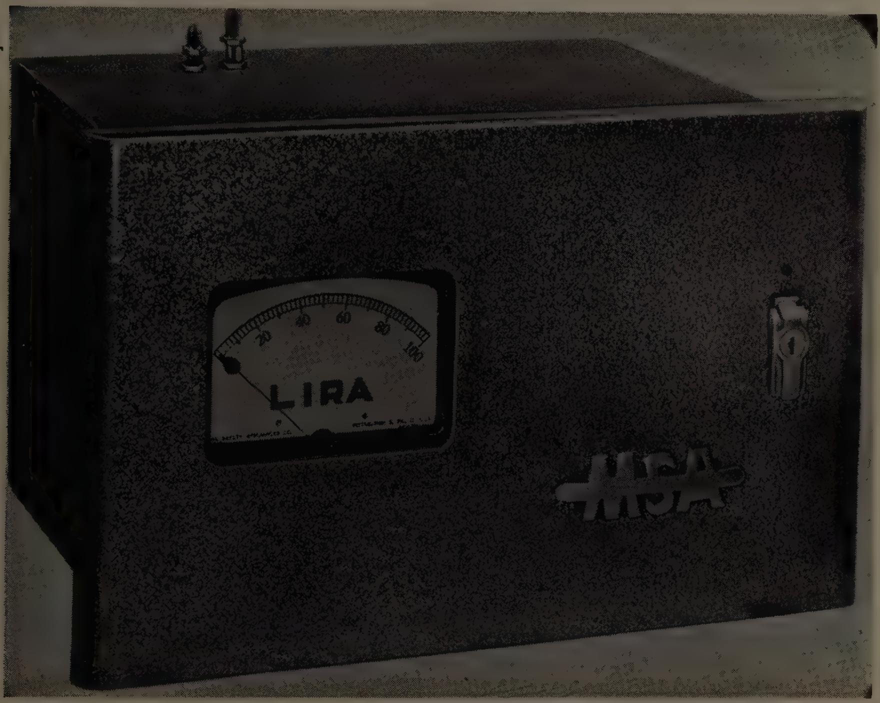


Figure 9.

Thermal Conductivity and Convection Effects

The technique of detecting and measuring the concentration of certain gases in air or other atmospheres by observing their effect on the heat lost from a hot-wire filament is quite old and well covered in the literature. Probably the first application of this method was to the surveillance of hangar atmospheres in the early days of hydrogen-filled balloons.

Although this measurement principle works well for binary mixtures, it has limitations in multicomponent atmospheres because of the many combinations of concentrations that can have the same thermal conductivity. Sample conditioning, such as removal of an interfering compound or saturating the sample at a constant temperature, aid in extending the applicability of the method.

FIGURE 10.

Heat is lost from a hot filament by several routes. In the instruments commonly referred to as thermal conductivity devices, the cell in which the filament is exposed to the tested atmosphere is purposely shaped to emphasize the conductivity effect and to minimize convection, radiation, and metal to metal conduction.

To obtain specificity for a particular component, it is possible to make use of the convection effect on filaments located electrically in other arms of the Wheatstone bridge measuring circuit. An approximate equation governing the rate of heat loss from a cylindrical element in a cylindrical cell is helpful in applying the compensating technique.

$$H \sim Ak\left(\frac{cd}{vk}\right)^{m} + Bk(T_2 - T_1) + C$$

where H = rate of heat loss, k = thermal conductivity of the mixture, c = specific heat of the gas at constant pressure, d = density, v = viscosity, A and B are constants depending on the cell dimensions, m is a cell shape factor, and C is a constant including radiation and end losses.

The first term is the contribution of convection, the second that of conduction. These terms show the relative influences of various physical properties of the gas. The radiation and end losses are substantially constant under the conditions in which the detector cells operate.

FIGURE 11.

To make an analyzer specific for one gas in a multicomponent mixture, the equation can be used as a guide in enhancing the effects of that gas on one arm of the bridge while maintaining equal the net effect of the background gas on all arms.

An interesting example of the application of these principles is the measurement of ethylene oxide in CO_2 and in mixtures of CO_2 and air. Ethylene oxide is used as a sterilizing agent and is rendered safe for handling by diluting with CO_2. High-pressure cylinders are filled with the desired mixture. Because of the different vapor pressures of the two compounds, special eduction tubes are used to obtain a fairly constant ratio as the mixture is used from the cylinder.

In practice, a sterilization chamber is partially evacuated and refilled with the mixture from the cylinder. It is therefore desirable to be able to measure the concentration of C_2H_4O in either CO_2 as it comes from the supply tank or in the sterilizer atmosphere where an unknown amount of air might be present.

FIGURE 12.

FIGURE 13 shows the cell block and filaments chosen. FIGURE 14 shows the response of the *A* filaments to various mixtures of C_2H_4O, CO_2, and air. Response is influenced by the CO_2 to air ratio and is higher at high CO_2 concentrations.

FIGURE 15 gives the response of the *B* filaments to similar mixtures at two filament temperatures. The slope of the curves shift as shown as the filament temperature varies. This filament and cell configuration give greater response for low CO_2 concentrations. By combining the two types of filaments in a four-arm bridge and selecting the optimum filament temperatures, it should therefore be possible to achieve selectivity to C_2H_4O.

FIGURE 16 demonstrates that this assumption is correct since the combination responds to the concentration of C_2H_4O present and ignores changes in background gas from a 50–50 air-CO_2 mixture to 100 per cent CO_2.

The significance of this illustration is not as much the solution of the individual problem as the fact that simultaneous use of more than one physical property often provides a means of producing an analyzer with selective response. Density, viscosity, and specific heat enter into the transfer of heat by convection. Because CO_2 and C_2H_4O have the same molecular weight, 44, it is the difference in viscosity that is combined with thermal conductivity in this analyzer.

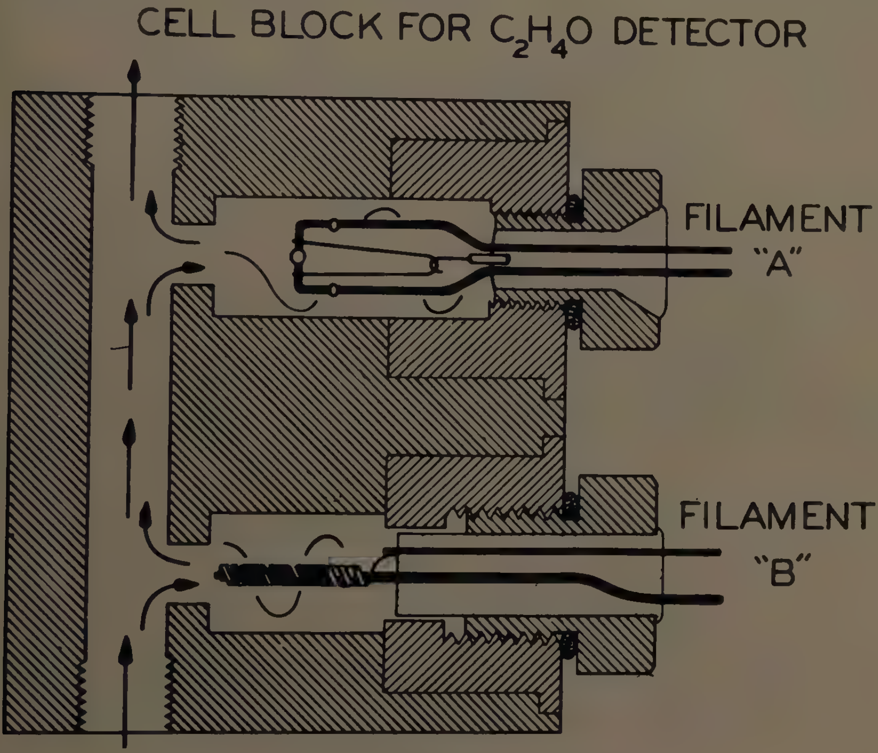


Figure 13.

Ionization Phenomena

Several ionization properties of gases are now being exploited to produce very sensitive analyzers. It has been known for a long time that a flame, burning hydrocarbons, becomes conductive because of the ionized or excited molecules produced. This fact has been recently adapted to the measurement of carbon-bearing compounds in air or in the effluent gas of chromatographic separation columns. The method has a wide range of sensitivity from a few parts per million to several volume per cent. For very sensitive applications, high purity hydrogen and oxygen or air must be used to provide the flame.

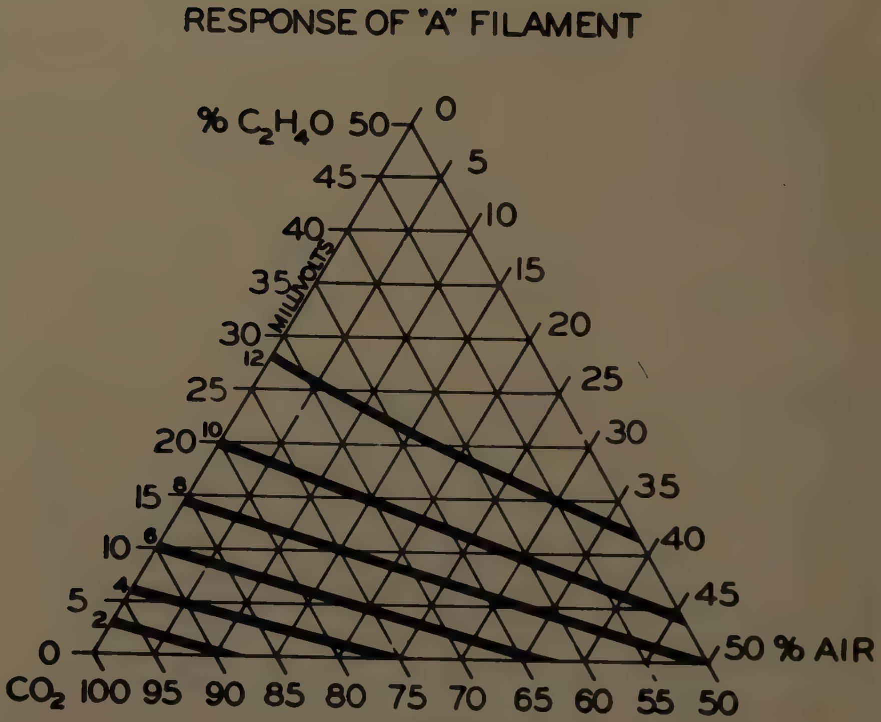


FIGURE 14.

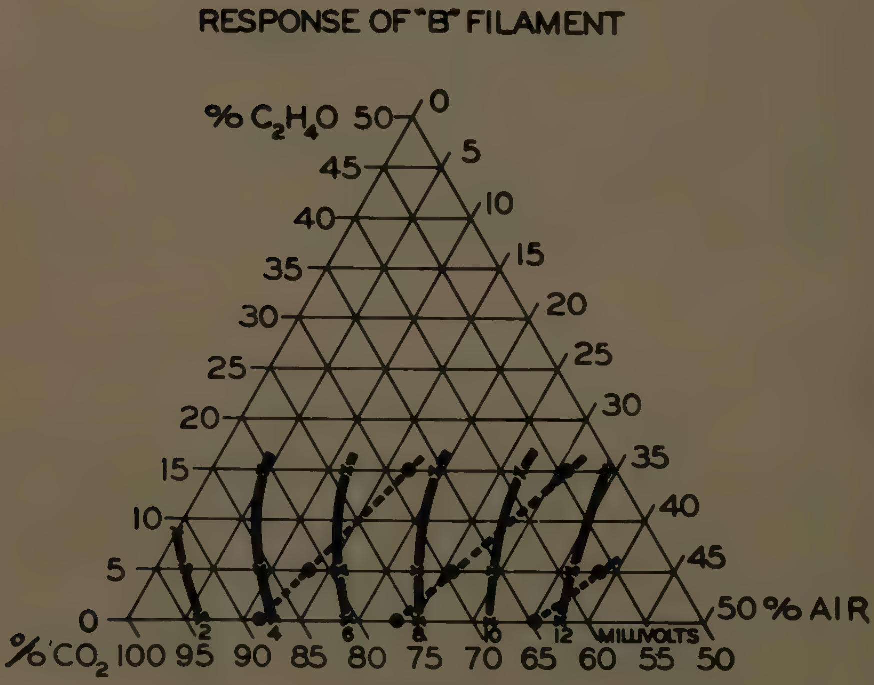


FIGURE 15.

An unique application of ionization phenomena is an instrument that employs the removal of ions or electrons from an ionization chamber due to the presence of the compound detected.

FIGURE 17 shows the general construction of the ion chamber detector.

A small radium source is used to ionize the chamber atmosphere, and current is measured with an electrometer type circuit. The outer wall of the chamber forms one electrode, which is held at ground potential. The central electrode insulator support is heated preserving high insulating properties even when moist atmospheres are drawn through the cell.

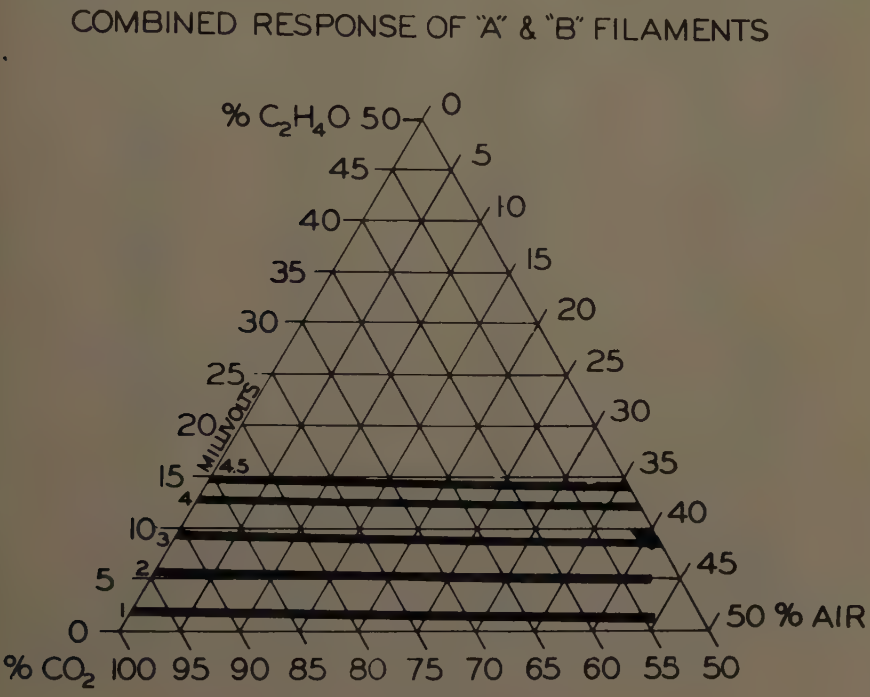
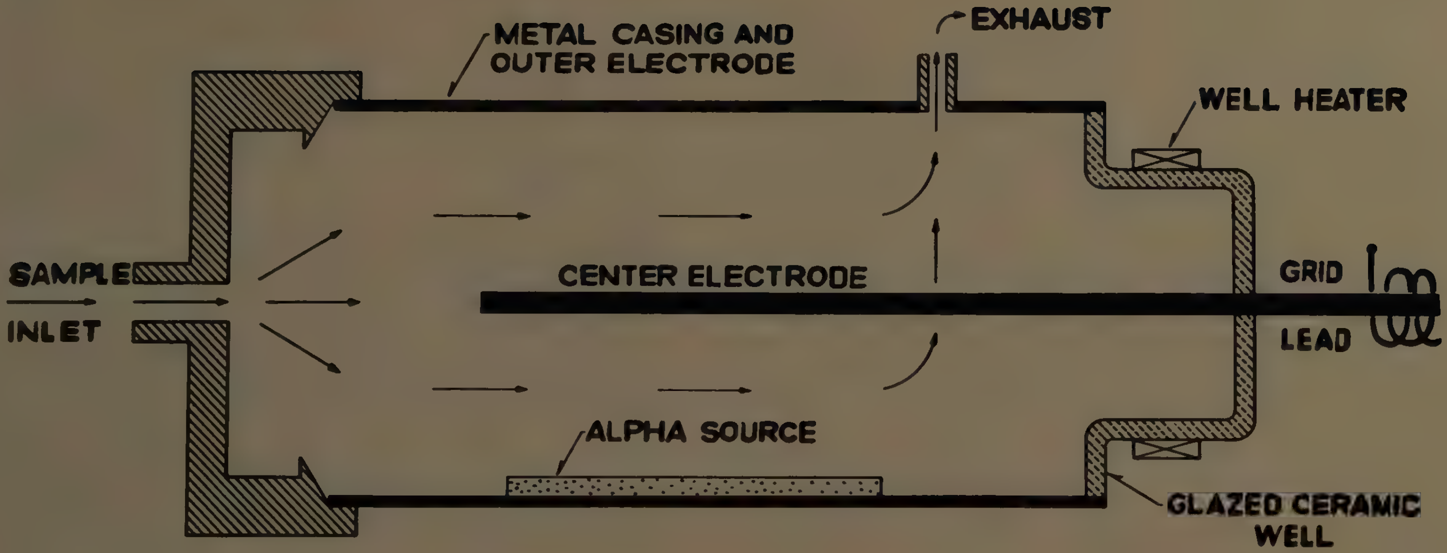

COMBINED RESPONSE OF "A" & "B" FILAMENTS

FIGURE 16.

The affinity of molecules such as O_2 or CO for electrons enables them to be detected in nonelectron-attaching gases such as argon, hydrogen, or nitrogen. Concentrations as low as a few parts per million effectively immobilize the electrons formed by ionization of the argon and decrease the chamber current by several orders of magnitude.

Compounds that do not exhibit electron affinity can be detected by forming finely divided particulate matter from them by appropriate means such as chemical reaction, pyrolysis, or ultraviolet radiation. The particles effectively immobilize both electrons and ions formed in the chamber and thus decrease the measured current.

These instruments are being used in processes requiring high-purity argon or helium and around missile bases for the detection of fuels and oxidizers which are toxic in low concentrations. For example, HF and F_2 are detected



IONIZATION CHAMBER

Figure 17.

by reacting with NH_3 to form solid fluoride; NO_2 is reacted with ammonia or amines to form a nitrate.

Typical full scale ranges and sensitization methods are shown in TABLE 1.

Sampling Systems

The successful application of any process analyzer is greatly dependent upon an adequate and reliable sampling system. The stream to be analyzed may be at high or low pressure and temperature, may contain condensible compounds or entrained matter, may be saturated with water, may have a tendency to form polymers or may have other characteristics that make it difficult to present a representative sample to the analyzer. When the concentration of the compound of interest is in the parts per million or parts per billion range, it can become lost in the sampling system by adsorption, or by reaction with materials of the line, valves, regulators, or flow indicators, or it may be taken out by dryers or other sample-conditioning equipment. Temperature changes can affect adsorption and desorption rates to produce false signals due to holdup and subsequent release of the detected compound. Heat can cause breakdown of compounds such as tetraethyl lead or nickel carbonyl. It is therefore essential that the sampling system be carefully planned, using a maximum exchange of information between the instrument user and manufacturer.

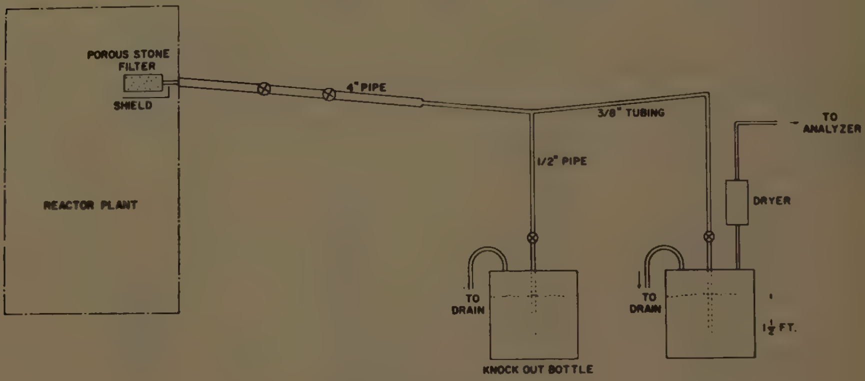
TABLE 1

COMPOUNDS DETECTABLE BY ION REMOVAL PHENOMENA AND PRACTICAL INSTRUMENT RANGE

Material detected	Sensitization method	Instrument range
Amines	HCl or NO_2 reagent	Low ppm
Ammonia	HCl or NO_2 reagent	0–50 ppb
Hydrazine	HCl or NO_2 reagent	0–50 ppb
UDMH	HCl or NO_2 reagent	Low ppm
CCl_4	CuO converter	0–10 ppm
Ethylene bromide	CuO converter	0–20 ppm
Ethylene chloride	CuO converter	0–50 ppm
SO_2	CuO converter	0–10 ppm
Tetrachloroethylene	CuO converter	0–20 ppm
Trichloroethane	CuO converter	0–20 ppm
Trichloroethylene	CuO converter	0–20 ppm
Chlorine	NH_3 reagent	Low ppm
Fluorine	NH_3 reagent	0–5 ppm
Hydrogen chloride	NH_3 reagent	0–50 ppb
Hydrogen fluoride	NH_3 reagent	0–5 ppm
Nitrogen dioxide	NH_3 reagent	0–10 ppm
Phosgene	NH_3 or CuO	Estimate ppm
HCN	HBr	0–20 ppm
Nickel carbonyl	Pyrolysis or UV radiation	0–50 ppb
Tetraethyl lead	Pyrolysis or UV radiation	0–50 ppb

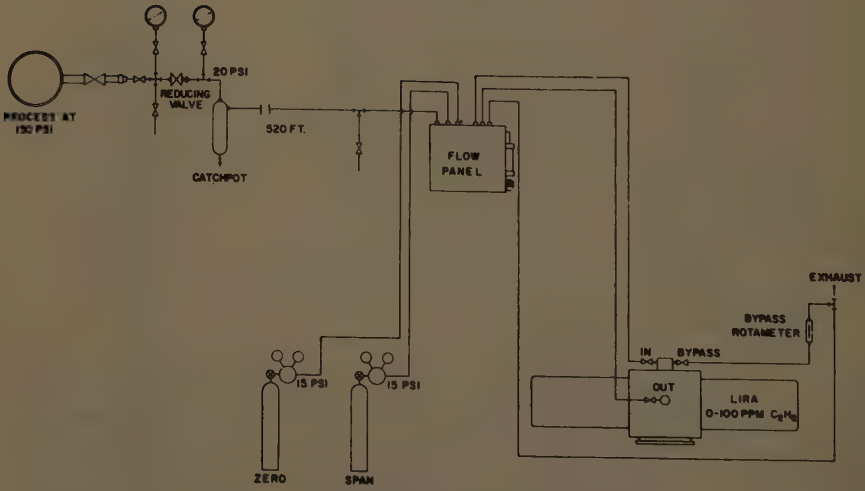
Some illustrations of sampling systems used may be of interest. FIGURE 18 shows a simple system for removal of dirt and excess water. FIGURE 19 is an installation for monitoring C_2H_2 in an ethylene process. Zero and span gas are provided for checking the instrument calibration.

Sometimes it is necessary or desirable to make controlled changes in the character of the sample. Such is the case in analyzing for hydrocarbons in liquid oxygen. The LOX is vaporized under conditions to prevent fractionation. The vapor is then passed through a catalytic oxidizer to convert all hydrocarbons to CO_2. The infrared instrument, which can be made very sensitive to CO_2, produces a reading in proportion to the total hydrocarbon contamination of the LOX.



SAMPLING SYSTEM FROM REACTOR PLANT

FIGURE 18.



SAMPLE SYSTEM FOR ETHYLENE PLANT

FIGURE 19.

Automatic periodic checks on the operation of the system are provided by a programmer that switches in pure O_2 for zero test gas, or a known hydrocarbon oxygen mix ahead of the oxidizer, or known CO_2 concentrations directly into the analyzer.

Summary

It has not been possible to discuss in detail many of the physical or chemical principles now being used in atmosphere analyzers. Those chosen are representative in that they have broad application or are of interest because they possess high sensitivity.

In the automatic analysis of atmospheres, it is not sufficient to consider the detecting and analyzing equipment alone. The entire system of obtaining a representative sample, of presenting it to the analyzer in suitable form, of disposing of used, reacted, or by-passed streams, and of checking instrument performance periodically must be carefully designed to assure satisfactory results.

Instrumentation for automatic analysis of process atmospheres has been developing at a rapid rate in recent years. Many physical and chemical principles are used, preference being given to physical measurements that require the use of no expendable reagents. Instruments based on measuring variations in thermal conductivity, density, heat of combustion, absorption of infrared or ultraviolet energy, and ionization properties are the most widely used. Specificity for selected stream constituents is sometimes achieved by chemical pretreatment or by simultaneous measurements of more than one property of the sampled atmosphere. Instrument full-scale calibrations range from a few parts per million to 100 per cent of the compound of interest depending on the application and principle of operation employed. The most generally used equipment has been reviewed, attention being given to principle of operation, typical application, advantages, limitations, and complexity.

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